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SYNTHESIS AND PERFORMANCE OF NOVEL AZO INITIATORS WITH SPECIAL REFERENCE TO EMULSION POLYMERISATION

A thesis submitted to the Council for National Academic Awards
in partial fulfilment of the requirements for the degree of
Doctor of Philosophy

by

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May 1984

ERRATA

p. 11: Eight lines up from bottom: anionic should read nonionic.

p. 24: After Eq. (2.2): The quantity n/V is not the concentration of free radicals in a locus, but the number of free radicals per unit volume in a locus.

p. 27: Reference (5) should read reference (51).

p. 49: Section 3.3, line 3: The name should read Verwey, not Verway.

p. 58: Last line: The reference Jackel (112) should read Jackel, as quoted in Ottewill and Walker (112).

p. 68: Sixth line after (III): The quantity is 0.07 μm, not 0.07 μ.

p. 80: Second line: Burker should read Bruker.

p. 84: Bottom: The formula should read $RO_2CCH_2CH_2C(CN)(CH_3)N{=}NC(CN)(CH_3)CH_2CH_2CO_2R$.

p. 93: Paragraph beginning 'Haines and Waters', line 3: The empty brackets should read (±).

p. 96: Sixth line from bottom: condensor should read condenser.

p. 98: Section 5.7.5.2, lines 4 and 11: knowun should read known.

p. 99: After equation: The empty space should contain the symbol ρ.

p. 138: Paragraph 2, line 1: ^{13}C NMR should read Proton NMR.

p. 142: Paragraph 2, line 3: -keto should read α-keto.

p. 179: Vertical axes: D should read D_∞ throughout.

p. 217: Line 6: polymrisation should read polymerisation.

p. 231: Last paragraph, first line: The word involves should be inserted after the word technique.

p. 233: Table 7.6: In the column headed 'Electron microscope', the symbol ± should be inserted between the first and the second number in each case.

p. 240: Page number missing.

p. 249: Second paragraph, line 10: solubl should read soluble.

p. 250: Second paragraph, line 2: $FA(EO)_{60}Es$ should read $FA(EO)_{30}Es$.

p. 257: First paragraph, line 10: $FA(EO9_{24}Es$ should read $FA(EO)_{24}Es$.

p. 259: Table 7.11: Last two columns should be headed $[M]_1$ and $[M]_2$, respectively.

p. 263: Equation: Division line missing.

p. 266: Second paragraph, line 2: iniiator should read initiator.

p. 284: Ref. (160): A. S. Hassan should read S. A. Hassan.

p. 285: Ref. (188): The year should be (1950), not (1980).

ABSTRACT

SYNTHESIS AND PERFORMANCE OF NOVEL AZO INITIATORS WITH SPECIAL REFERENCE TO EMULSION POLYMERISATION

by

F. BARRUTIA

Derivatives of 4,4'-azobis-4-cyanopentanoic acid were prepared using its diacid chloride and various hydroxyl and amino compounds. The objective was to obtain substances that would act both as initiators for different modes of free-radical polymerisation and also as stabilisers for emulsion polymerisation reactions carried out in the absence of added conventional surfactant. During the preparation of the above compounds, it was discovered that 4,4'-azobis-4-cyanopentanoyl chloride appears to exist in two different forms called I and II. These forms yielded two different forms of esters when reacted with straight-chain aliphatic alcohols. These esters are called 'esters A' and 'esters B', respectively. Surprisingly, the esters A were found to act as effective initiator/stabilisers for the emulsion polymerisation of styrene in the absence of conventional surfactant. Unfortunately, during the course of the investigation, it was suddenly found to be impossible to prepare further batches of acid chloride I, and most subsequent attempts to prepare acid chloride I met with failure. The efforts which had been made to try to prepare acid chloride I and to elucidate possible structural differences between I and II that might account for the observed phenomena are described in detail.

The rest of this work is concerned with the study of the behaviour of esters derived from acid chloride II and a range of fatty-alcohol ethoxylates. Results are given for the use of these derivatives as both initiators and stabilisers for the emulsion polymerisation of styrene in the absence of added conventional surfactant. The effects of temperature, initiator concentration and the total volume of water upon the rate of polymerisation were studied. Also, the effects of these variables upon the shapes of the conversion-versus-time curves obtained when the esters were used as initiator/stabilisers were investigated. The surfactant properties of some of the initiator/stabilisers have also been investigated. The kinetics of the decomposition of these initiator/stabilisers is also included.

Advanced studies undertaken in connection with the programme of research in partial fulfilment of the requirements of the degree:

1. A course of postgraduate lectures and tutorials on the theory of the stability of lyophobic colloids.

2. A course of guided study on theories of emulsion polymerisation.

3. A symposium organised by the Royal Society of Chemistry in December 1981, entitled "Advances in Emulsion Polymerisation".

4. A symposium held at the National College of Rubber Technology, Polytechnic of North London, on 4th and 5th June 1981, entitled "Developments in Polymer Latices".

ACKNOWLEDGEMENTS

I would like to thank my supervisor, Dr. M. G. O'Brien, for his patience and for allowing me to carry the investigation into areas which I found particularly interesting.

Without the support and encouragement of Dr. D. C. Blackley, my second supervisor, and Dr. A. C. Haynes, a colleague and friend, it would hardly have been possible for me to overcome the various obstacles I encountered and hence to finish this investigation at all; moreover, I learned as much from them as from conducting the research: to both of them I am forever indebted.

Because of the unusual complexity of certain aspects of this investigation, I was obliged to seek assistance from a number of people as well as my supervisors; all of the following generously gave me their time: Dr. J. Charalambous, Dr. J. Glazer, Dr. H. R. Hudson and Dr. R. Twaits.

I was also obliged to seek help from the technicians of several departments of the Polytechnic; to all who gave me the benefit of their time and their skills I am very grateful. If I may single out one of them for special gratitude, it must be Ms. J. S. Kotiyan, who undertook the considerable task of obtaining a vast number of electron micrographs for me.

I am very grateful to Dr. S. Holding of RAPRA, who carried out molecular weight determinations on my behalf, and to the manufacturers of the Coulter Nanosizer, Coulter Electronic Ltd., who allowed me to use their instrument to determine particle diameters.

Of course, I am very grateful to the Inner London Education Authority and to the Polytechnic of North London for providing the financial support which made this work possible.

Finally, I would like to thank Dr. R. L. Trask for his endless hours spent editing and typing this thesis.

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CHAPTER ONE

INTRODUCTION TO EMULSION POLYMERISATION

1.1. Introduction to polymerisation. Polymerisation is a process by which a very large covalent structure is constructed from simple compounds. The molecular sizes involved are usually thousands of molecular weight units. Large molecular structures can be synthesised by two main processes:

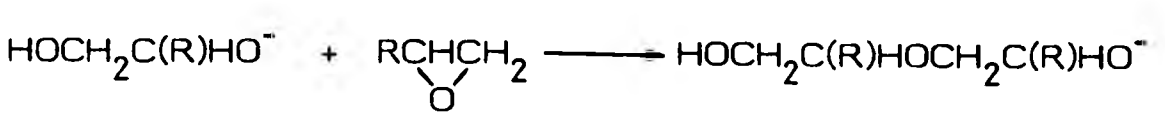
(1) condensation polymerisation;

(2) addition polymerisation.

Condensation polymerisation[1] takes place by a step-growth mechanism and the reactions involved are entirely analogous to condensation reactions in low molecular-weight compounds. In polymer formation the condensation takes place between two polyfunctional molecules, with the elimination of a small molecule, such as water.

Addition polymerisation involves a chain-growth mechanism in which the chain carrier may be an ion or a free radical. Addition polymerisation via an ion can be either cationic or anionic. An example of anionic polymerisation is the ring opening of ethylene oxide to form polyethylene oxide.

Substituted ethylene oxides react in the same way:



Cationic polymerisation occurs when the chain carrier is a carbonium ion. Typical catalysts for cationic polymerisations are Lewis acids and Friedel-Crafts catalysts such as aluminium chloride and aluminium bromide. All these catalysts are strong electron acceptors,

$$BF_3 + H_2O \longrightarrow H^+ + (BF_3OH)^-$$

enabling the monomer to acquire a proton, e.g.,

$$H^+ + (CH_3)_2C{=}CH_2 \longrightarrow (CH_3)_3C^+$$

Anionic polymerisation occurs when the chain carrier is a carbanion. The conventional method of initiation of ionic chains involves the addition of a negative ion to the monomer with the opening of a bond or ring, e.g.,

$$NH_2^- + CH_2{=}CHX \longrightarrow H_2NCH_2CHX^-$$

Addition polymerisation can also be accomplished using free-radical chain carriers. The free radical is capable of reacting to open the double bond of an unsaturated monomer and adding to it, with an electron remaining unpaired. In a very short time, many more monomers add successively to the growing chain until two free radicals react to annihilate each other's growth activity.

Like all free-radical chain reactions, free-radical addition polymerisation of unsaturated carbon compounds can be envisaged as occurring via three principal steps, namely (1) initiation, (2) propagation and (3) termination.

The initiation step is the stage of the reaction during which active centres are being generated. In the propagation steps, these active centres grow. The termination step is the stage of the reaction in which the active centres are destroyed. The overall reaction may be complicated by various transfer reactions, depending upon the reaction conditions. The stages of a free-radical polymerisation can be represented as follows:

(1) Initiation: the formation of free radicals:

$$I \xrightarrow{k_i} 2\,R\cdot$$

(2) Propagation: the rapid addition of monomer molecules to the active centre:

$$R\cdot + M \xrightarrow{k_p} RM\cdot$$
$$RM\cdot + M \xrightarrow{k_p} RMM\cdot \text{ etc.}$$

where M represents a molecule of the unsaturated monomer.

(3) Termination: the neutralisation of the active centre. This step can have two different outcomes:

(a) combination, in which two radicals combine to give one molecule; e.g.,

$$R(M)_nM\cdot + R(M)_mM\cdot \xrightarrow{k_t} R(M)_nMM(M)_mR$$

(b) disproportionation, e.g.,

$$R(M)_nM\cdot + R(M)_mM\cdot \xrightarrow{k_t} R(M)_nM' + R(M)_mM''$$

where M' denotes a monomer unit to which a hydrogen atom has been added, and M'' denotes a monomer unit containing a double bond.

(4) Transfer of a radical. This can occur

(a) to modifier (HX) -- in some cases this may be the solvent; in others it is an added substance:

$$R(M)_nM\cdot + HX \longrightarrow R(M)_nMH + X\cdot$$

(b) to monomer (M):

$$R(M)_nM\cdot + M \longrightarrow R(M)_nMH + M\cdot$$

(c) to polymer (P):

$$R(M)_nM\cdot + P \longrightarrow R(M)_nMH + P\cdot$$

(d) to initiator (I):

$$R(M)_nM\cdot + I \longrightarrow R(M)_nM + I\cdot$$

Practically, free-radical polymerisation can be carried out in several ways.

(1) An initiator may be added to the monomer and the polymerisation carried out in bulk. With this procedure, there are problems of exotherm from the reaction and the increasing viscosity of the polymerisation mixture as polymerisation proceeds. To overcome these problems of exotherm and high viscosity, a dilution medium is usually employed.

(2) The polymerisation can be carried out in a suitable solvent. It is then possible that the temperature of the reaction can be controlled by allowing the solvent to boil.

(3) The polymerisation can be carried out with the monomer droplets suspended in an aqueous medium, yielding the polymer in the form of beads which can be easily collected by filtration. The water removes the heat of polymerisation and facilitates stirring.

(4) The monomer can be emulsified with water. Again, the water controls the temperature and the viscosity. At the end of the reaction a latex is produced, i.e., a colloidal dispersion of polymer in water.

1.2. Introduction to the mechanism of emulsion polymerisation. "Emulsion polymerisation" is the term which is used to describe one of the processes employed for some free-radical addition polymerisations of olefinic monomers[2]. Normally, this polymerisation process takes place in reaction systems which are in the form of emulsions, i.e., a dispersion of one liquid (in this case the monomer) in a second immiscible liquid[3], although it is not essential that the monomer be dispersed in this way. Blackley[4] defines emulsion polymerisation as "an addition polymerisation process in which the several concurrent propagating centres are isolated

from one another".

1.2.1. Qualitative picture of emulsion polymerisation. If one considers a highly idealised emulsion polymerisation system, it will contain certain ingredients. These ingredients, with typical proportions, are as follows:

Ingredient	Parts by weight
Dispersion medium	150
Monomer	100
Emulsifier	5
Initiator	0.5

The dispersion medium is usually water. The emulsifier is not essential, although it is a usual ingredient to add to emulsion polymerisation reactions.

An emulsifier is a surface-active substance whose molecules usually comprise two distinct regions: one is a polar hydrophilic region which has an affinity for the aqueous medium, and the other is a non-polar hydrophobic region which is water-repellent. When a small portion of the surface-active agent is dissolved in the water, the bulk of the emulsifying molecules may aggregate together to form small colloidal clusters known as "micelles". In these micelles the hydrophobic regions are orientated towards the interior of the micelle and the hydrophilic regions are orientated towards the water. An average emulsifier micelle will have a diameter of approximately 5 nm, and is thus of colloidal dimensions. These aggregates are only formed when the concentration of surfactant in solution exceeds a certain value. This value is known as the critical micelle concentration (c.m.c.).

The initiator is the moiety that undergoes decomposition either thermolytically or by a redox-activated mechanism, producing primary radicals. Typically radicals are produced at the rate of ca. $10^{13} ml^{-1} s^{-1}$ at $50^{0}C$. This rate remains steady throughout the polymerisation as the half-life of typical initiators far exceeds the duration of the polymerisation reaction. Different kinds of initiators are used; e.g., redox

systems, azo initiators, persulphates, and peroxides. The most efficient initiators for emulsion polymerisation are those which are soluble in water. Efficient stirring is desirable for at least the earlier stages of emulsion polymerisation. When such a system is studied, the emulsion polymerisation is carried out at constant temperature, since the rates of most chemical reactions are temperature-dependent. Because oxygen can affect the rate of polymerisation, an inert atmosphere, usually nitrogen, is often established above the reaction system. At the end of the reaction, a latex is produced, i.e., a colloidal dispersion of polymer in water. The size of the latex particles produced by emulsion polymerisation depends upon the recipe used. This could be between 50 nm and 500 nm, but is often in the range 50-150 nm.

Distinct stages -- or "intervals" -- of an emulsion polymerisation reaction are often revealed by examining the curve of conversion vs. time. Figure 1.1 illustrates the shape of the curve which is often obtained. It reveals that the reaction is divided into three distinct "intervals", known respectively as Interval I, Interval II and Interval III.

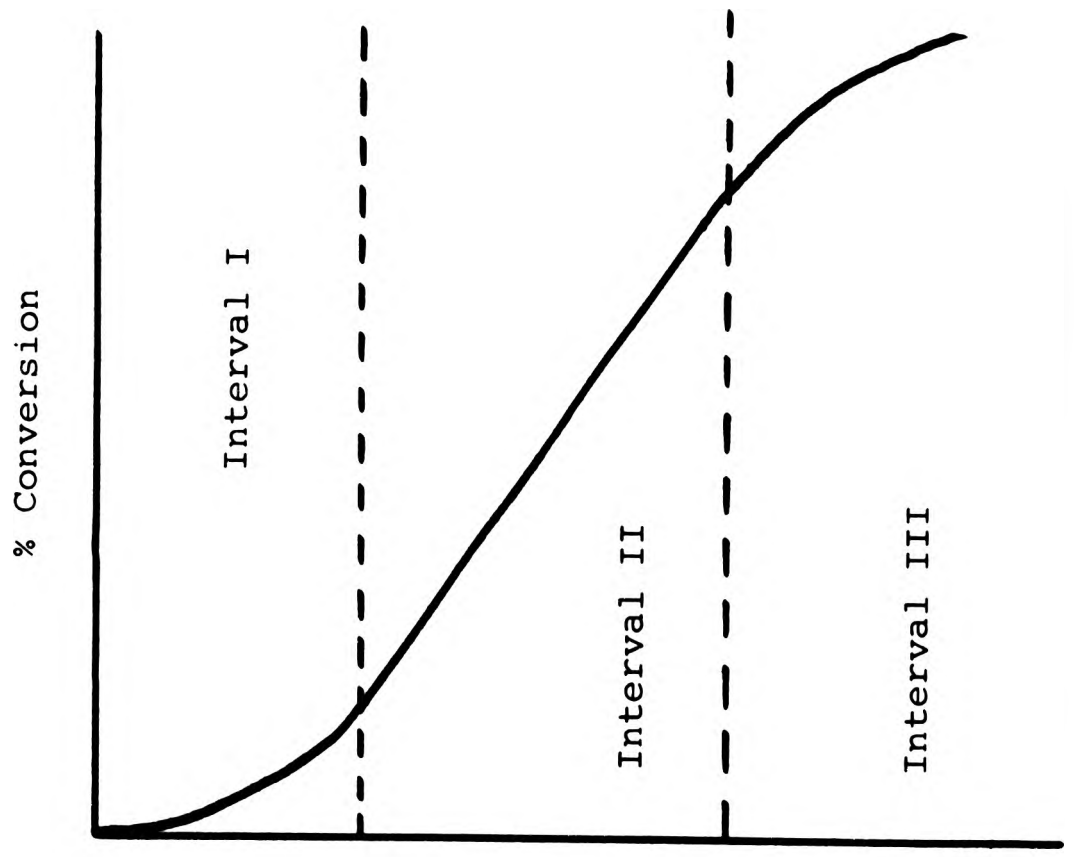


Fig. 1.1: A typical plot of extent of polymerisation against time of reaction for an emulsion polymerisation reaction.

Interval I: This is the initial stage of the reaction. It is interpreted as the period of the reaction during which particle formation takes place. It is often referred to as the "particle nucleation" or "locus-nucleation" stage. The number of particles, and consequently the polymerisation rate, increases during this interval, but eventually particle formation ceases (usually at less than 10% conversion). Thereafter, all radicals generated are captured by existing particles.

Interval II: The second interval begins when the number of loci reaches its maximum and becomes constant. It normally lasts from the end of Interval I until the monomer droplets disappear as a separate monomer phase. This second interval is characterised by a constant rate of polymerisation, and, in the absence of agglomeration, the number of particles is commonly believed to be constant. The monomer concentration in the particles is also believed to be approximately constant at an equilibrium value which is determined by the size of the growing particle[5], so long as a separate monomer-droplet phase remains. The reaction is first-order with respect to monomer concentration during Interval II; i.e., the rate is proportional to the monomer concentration. Interval II often extends from approximately 10% to about 60% conversion. The end of Interval II occurs when the monomer droplets disappear as a separate phase.

Interval III: The third interval begins when there is no more monomer to diffuse through to the growing polymer. Therefore monomer becomes depleted within the particle during this stage of the reaction. Finally polymerisation will cease completely when all the monomer in the particles has been used up; indeed in some cases it virtually ceases before all the monomer has polymerised. The rate of disappearance of monomer would be expected to be first-order with respect to monomer concentration during Interval III, but the rate of termination may fall to such an extent with increasing viscosity of the particles that a gel effect may be observed. This will cause a decrease in the termination rate and thus an increase in the molecular weight.

The physical state of the emulsion polymerisation reaction system makes it easy to control the polymerisation process. Thermal and viscosity

problems are much less significant than in bulk polymerisation. Emulsion polymerisation is also a useful process in that it affords a means of increasing the polymer molecular weight without decreasing the polymerisation rate.

It is observed that the molecular weight of the polymer obtained by emulsion polymerisation is usually considerably higher than that obtained by a bulk polymerisation proceeding at the same rate and at the same temperature. The reaction in an emulsion polymerisation occurs much more rapidly than in the bulk at the same overall rate of initiation, and the degree of polymerisation of the product of emulsion polymerisation is nearly five times greater than that of the product of bulk polymerisation carried out under comparable conditions. To a large extent, the molecular weight and polymerisation rate can be varied independently of each other.

It is also observed that the surface free energy of the air-aqueous phase interface undergoes an increase at a certain stage in the reaction. Because of these differences in molecular weight and polymerisation rates, the mechanism of an emulsion polymerisation reaction must differ in some way from that of the bulk, solution and suspension polymerisation systems. What is the reason for these differences between emulsion polymerisation systems and other types of polymerisation systems?

According to one theory, when the surface-active agent is dissolved in the water, the bulk of the emulsifying molecules aggregate together to form micelles. If a water-insoluble monomer is added to this system, a very small fraction of the monomer dissolves and goes into solution in the water. As only a very small portion of the monomer dissolves in the water, polymerisation in the water phase is unlikely to occur to any great extent. This does not apply to monomers of high solubility in water. A larger, but still small, portion of the monomer enters the hydrophobic interior of the micelles. This is known as solubilisation. Because of this, many non-polar substances which are almost insoluble in water appear to be more soluble in aqueous solutions of surface-active substances. According to this theory of emulsion polymerisation, solubilisation is of critical importance, since it is believed that initially polymerisation takes

place inside these solubilised clusters. But a large part of the monomer is dispersed as monomer droplets that are believed to be stabilised by emulsifier adsorbed on their surfaces. The droplet size of the original dispersed monomer is at least one order of magnitude greater than the final latex particles. Experiments have been carried out to show that the monomer droplets are not an important locus of polymerisation, at least when water-soluble initiators are used. However, it is known[6] that under certain conditions, namely (1) that the monomer contains dissolved polymer, (2) that an oil-soluble initiator is used, and (3) that the monomer droplets are small[7] and numerous, monomer droplets can be the principal loci of reaction.

In the ideal system, it is assumed that the initiating free radicals are generated exclusively in the water phase. Within a very short time, radicals will meet the monomer-swollen micelles in which the polymerisation then starts. After initiation, therefore, a new phase is produced, namely, a polymer latex particle swollen with monomer. The monomer within the micelle is quickly used up, and more monomer diffuses into the micelle from the surrounding water phase. In order to maintain equilibrium, monomer diffuses out of the monomer droplets and goes into solution. Thus the principal function of a monomer droplet is to act as a reservoir of monomer from which it can diffuse through the water phase to the growing latex particles.

After initiation, polymerisation inside the micelles proceeds rapidly and the latex particles grow from within. Increasing amounts of emulsifier are adsorbed on the surface of the growing latex particles. This emulsifier functions as a colloidal stabiliser, preventing the latex particles from flocculating; i.e., the adsorbed layer which surrounds the particles prevents them from coagulating to form the thermodynamically more stable flocculated state. This in turn tends to cause the remaining micelles to dissociate, their molecules in consequence dissolving in the water phase. Thus, as polymerisation proceeds, micellar soap becomes adsorbed soap. Finally no micelles are left, since the concentration of emulsifier in the aqueous phase has been reduced to below the critical micelle concentration. At this point, the surface free energy of the air-aqueous phase interface increases. According to conventional theories of

emulsion polymerisation, at this point the number of latex particles is fixed and further polymerisation occurs only inside the latex particles.

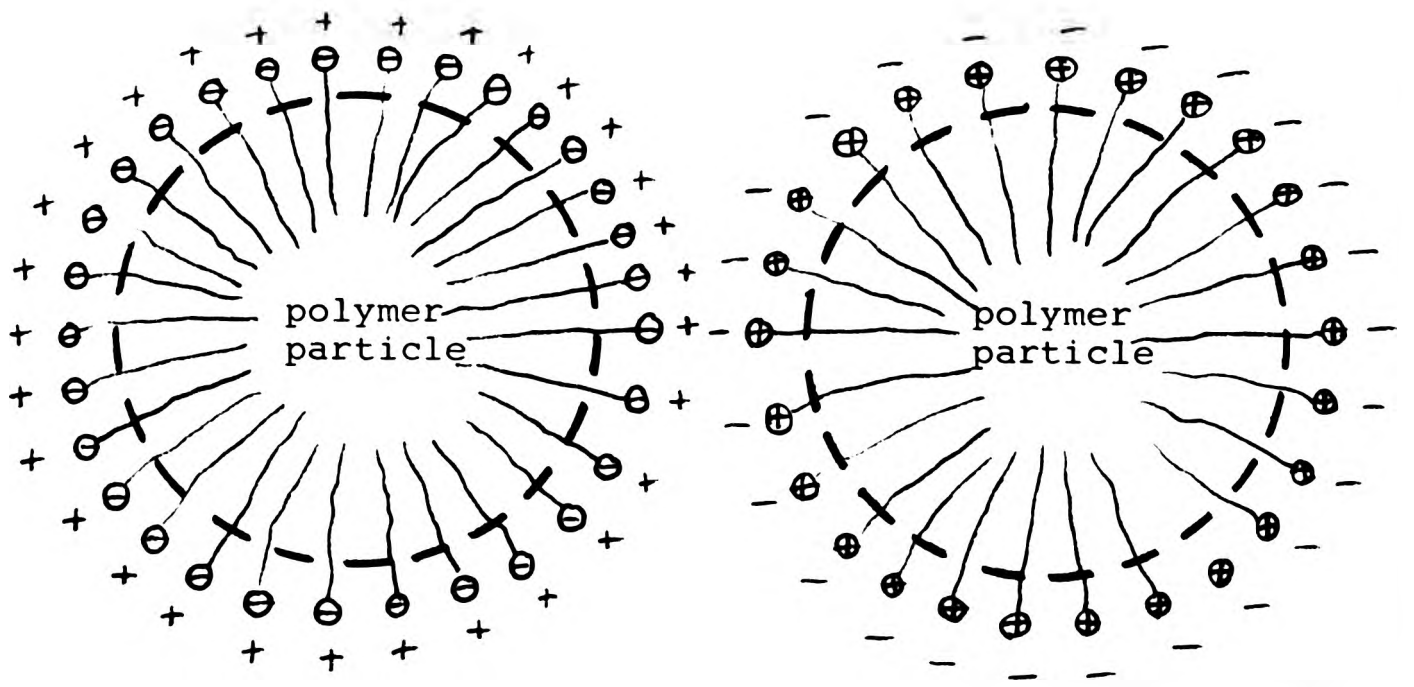
Although the theory that particle nucleation occurs by the micellar mechanism is attractive and accounts for some of the experimental observations, it can not explain why emulsion polymerisation occurs in the absence of added surfactant. The mechanism of particle formation under such circumstances and also for relatively water-soluble hydrophilic monomers is believed to be what is now generally called "homogeneous nucleation". According to this theory, polymerisation initially takes place in aqueous solution. This is followed by precipitation of the polymer in a colloidal form. During the early stages of polymerisation, soluble oligomeric free radicals exist in solution. These would ultimately grow to some critical size above which they would precipitate out to form primary particles in which the subsequent polymerisation takes place.

The growing latex particles are continually supplied with monomer which diffuses through the aqueous phase from the monomer droplets. These droplets gradually decrease in quantity as the polymerisation proceeds, until at a conversion of about 60% they disappear completely. From this point on, the monomer in the latex particles is gradually used up and the rate of conversion of monomer to polymer will gradually fall off until no further appreciable reaction is taking place.

1.3. Role of the surfactant in emulsion polymerisation reactions. Originally, it was believed that the main function of the surfactant in emulsion polymerisation reactions was to provide micelles in which nucleation of particles could occur. The secondary functions of imparting colloidal stability to the particles and of helping to emulsify the monomer droplets were also recognised. When particle nucleation occurs in the absence of micelles, and when the concentration of added surfactant is insufficient to form micelles, the likely major role of the added surfactant is to stabilise the particles and the polymer molecules from which they are formed.

Surfactants can be generally divided into two main groups: (i) ionic, and (ii) non-ionic. Ionic surfactants are anionic, cationic or amphoteric salts,

such as carboxylic-acid salts, quaternary ammonium salts, and compounds which have amino and carboxylic-acid groups in the same molecule[8]. Figure 1.2 shows how these ionic surfactants stabilise the polymer particles. Amphoteric surfactants contain both acidic and hydroxylic groups. They usually act as cationic surfactants in acid media and as anionic surfactants in alkaline media.[9]



Figs. 1.2a and 1.2b: Graphical representation of surfactant molecules surrounding polymer particles. Fig. 1.2a shows an anionic surfactant; Fig. 1.2b, a cationic surfactant.

Non-ionic surfactants comprise compounds such as the esters of polyalcohols and the ethoxylates and ethoxylate-propoxylates of alkyl and alkylaryl condensates, compounds which can contain one or more active hydrogen atoms. These compounds can exert the solubilising action described in section 1.2.1. above[10]. The most common anionic surfactants contain either an alkyl or an alkylphenyl group as the hydrophobic portion and a long polyoxyethylene or polyoxyethylene-propylene chain as the hydrophilic portion. The polar portion of such a non-ionic surfactant consists of a long, uncharged chain which is much bigger than the hydrophobic group. Therefore it is not surprising that the solution properties of these surfactants are quite different from those of the ionic surfactants from which the classical ideas of micellar behaviour

and structure were derived.

Possible structures for the micelles produced with non-ionic surfactants have been put forward by Dennis et al[11]. These include non-classical micellar structures, such as oblate ellipsoids, and classical spherical micelles, in which part of the polyalkylene oxide chain extends into the hydrophobic region, giving rise to a less well-defined interface region.

How stability is conferred on latices where only non-ionic surfactants are used will be discussed later when the theories of colloid stability are reviewed.

It can be deduced from the foregoing discussion that the balance between the hydrophobic and the lipophobic portions of the molecule will be crucial in determining the behaviour of non-ionic surfactants. Methods of measuring the hydrophobic-lipophobic balance (HLB) which can be used under certain conditions to check and measure the efficiency of non-ionic emulsifiers are described by Blonchard[12]. A definition of hydrophobic-lipophobic balance is given by Bourrel et al[13] as follows:

$$\text{HLB value} = \frac{\text{weight per cent ethylene oxide}}{5}$$

Non-ionic emulsifiers are used because they exhibit useful characteristics. The effectiveness of ionic emulsifiers can be dependent upon the pH of their environment, whereas the behaviour of non-ionic surfactants is virtually independent of pH. Another advantage of non-ionic emulsifiers is that they do not form insoluble precipitates in the presence of heavy metal ions. The disadvantage of non-ionic emulsifiers is that, while soluble at room temperature, they are often insoluble above a certain critical temperature. This inverse solubility phenomenon can be troublesome.

1.4. Emulsifier-free emulsion polymerisation. Although the role of a surfactant is important in conventional emulsion polymerisation reactions, the presence of an added surfactant is not essential for emulsion polymerisation to occur. Several workers, for example Goodwin et al[14], have obtained monodisperse polystyrene latices by emulsion

polymerisation in the absence of added surfactant, using potassium persulphate as initiator. The particles are stabilised as a colloidal dispersion by surface groups derived from the initiator. These groups are an integral part of the particle and are not removed by dialysis. Conductimetric titrations reveal the presence of sulphate, carboxyl and hydroxyl groups on the particle surfaces. Goodall et al[15] have studied the emulsion polymerisation of styrene in the absence of emulsifier, using a persulphate compound as initiator. They find nucleation and growth processes similar to those found during the initial stages of conventional emulsion polymerisation. In a subsequent paper, Goodall et al[16] discuss the mechanism of emulsion polymerisation of styrene.

In the case of surfactant-free emulsion polymerisations, the polymer content of the resultant latices is much lower than those of latices produced by conventional emulsion polymerisation (approximately 5% is typical of surfactant-free emulsion polymerisations) and the particles are large (ca. 500 nm is typical).

Fitch and Kasargod[17] have synthesised disodium-bis-(4-sulphomethylbenzoyl) peroxide, and this has been used as an initiator for the emulsion polymerisation of styrene in the absence of added emulsifier.

1.5. Initiation in emulsion polymerisation reactions. Initiation is defined as the process or processes by which a propagating centre is generated in an addition polymerisation reaction system. In emulsion polymerisation reactions, the initiating species can be formed by:

(a) the decomposition of initiator in the aqueous phase to yield initiator radicals;

(b) the reaction of initiator radicals with water molecules to form other radicals;

(c) the reaction of initiator radicals with monomer molecules dissolved in the aqueous phase;

(d) the transfer of radicals from the oligomeric propagating centres in the aqueous phase to the polymerisation loci.

If the initiator is oil-soluble, the production of initiating radicals can also occur in the monomer droplets. A great variety of initiators can be used

in emulsion polymerisation reactions. In all cases, the effectiveness of an initiator depends upon the liberation of active free radicals. These active free radicals are produced by either of two means:

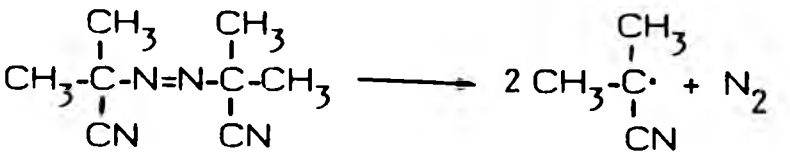
(1) By thermal decomposition of the initiator: The most commonly used initiators are those containing a peroxidic bond (-O-O-), where the initiation step takes the form $ROOR' \longrightarrow RO\cdot + \cdot OR'$.

One very important initiator which is widely employed in emulsion polymerisation is the persulphate ion, which may be used as the sodium, potassium or ammonium salt. It is represented as decomposing thermally to give sulphate ion radicals as the initiating species:

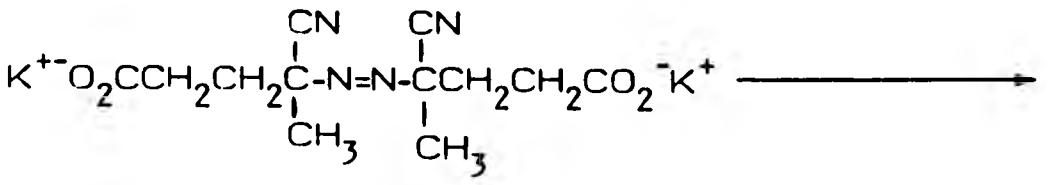
$$S_2O_8^{2-} \longrightarrow 2 \cdot SO_4^-$$

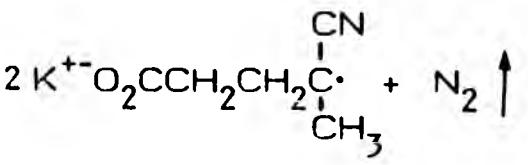
However, the production of sulphate groups is dependent upon the pH of the system[18].

No such restrictions apply to azo compounds. One commonly encountered initiator is 2,2'-azobisisobutyronitrile:



The above initiator is oil-soluble. An example of a water-soluble azo initiator is 4,4'-azobis-4-cyanopentanoic acid sodium or potassium salt:





The above initiator is water-soluble, and the rate of decomposition to give free radicals is independent of pH[19].

(2) By interaction between a reducing and an oxidising agent: These are known as "redox" initiating systems. They comprise two or more substances whose mutual interaction produces free radicals which are able to initiate polymerisation, e.g.,

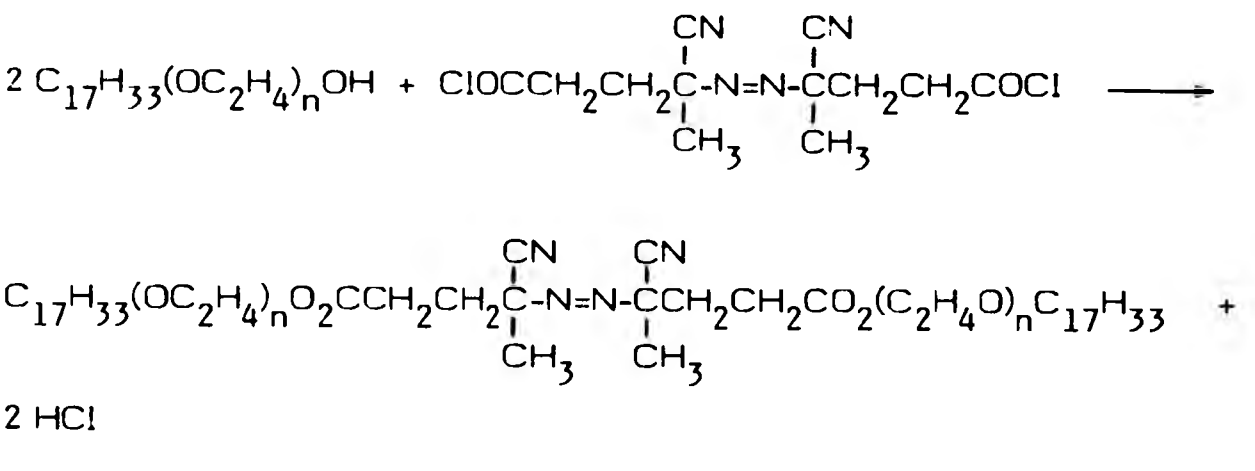
$$H_2O_2 + Fe^{2+} \longrightarrow HO\cdot + HO^- + Fe^{3+}$$

The production of free radicals alone is not the only consideration to be borne in mind when choosing an initiation system. The initiating species should have a solubility such that the distribution between the aqueous and the organic phase makes them available for initiation in the appropriate locus. If it is too water-soluble, the free radicals produced may have difficulty in reaching the locus of polymerisation. If it is too soluble in the organic phase, too many radicals may enter the swollen micelles and excessive termination may prevent polymer of high molecular weight from being formed.

1.6. Objectives and original plan of the present investigation. During a research project carried out previously[20], the writer discovered that certain straight-chain esters of 4,4'-azobis-4-cyanopentanoic acid not only acted as initiators of free radical polymerisation but also as stabilisers for latices produced by emulsion polymerisation of styrene in the absence of added conventional surfactant. It was clear that this was an interesting observation which merited further investigation.

The objective of this investigation was the synthesis of a range of compounds which might simultaneously function as emulsifiers and initiators for emulsion polymerisation reactions based upon derivatives of 4,4'-azobis-4-cyanopentanoic acid. Initially, straight-chain esters of varying chain length were synthesised by reacting 4,4'-azobis-4-cyanopentanoyl chloride with hydroxyl compounds. In order to investigate further the effect of structural variations, straight-chain esters were synthesised from various other hydroxyl compounds. Aromatic derivatives were also synthesised from aromatic compounds which contain various

numbers of hydroxyl groups. In addition, a range of esters derived from a range of commercial fatty-alcohol ethoxylates were prepared and evaluated. The ethoxylates used were those supplied by ABM Chemicals as the "Texofor A" series. They are ethoxylates derived from a mixture of cetyl and oleyl alcohols. The ethoxylates are therefore compounds in which two distinct regions can be distinguished: one hydrophobic, derived from the cetyl/oleyl alcohol, and the other hydrophilic, derived from the chain of ethylene oxide units. It is well-established that the ether chains act as a hydrophilic moiety.



Amides were also synthesised by reacting long-chain amines with 4,4'-azobis-4-cyanopentanoyl chloride. It was of interest to compare the results of the emulsion polymerisation of styrene using these compounds with those obtained using the straight-chain esters, since the only difference between the two compounds is an N-H linkage instead of an oxygen linkage. Amide acids were the next type of compounds whose preparation was attempted, since the sodium or potassium salt could be readily synthesised to give ionic, water-soluble compounds.

Finally the synthesis of derivatives of hydroxy acids was attempted. Once the hydroxy acids were obtained, the corresponding esters could be readily synthesised. The sodium or potassium salt would yield ionic derivatives.

An assessment was made of the effectiveness of all these compounds as initiators for

(1) bulk polymerisation of styrene;

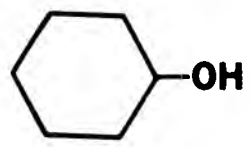
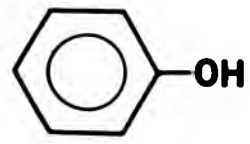
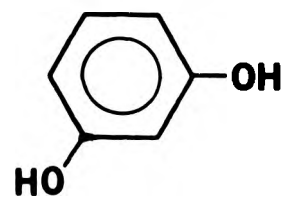
(2) conventional emulsion polymerisation of styrene, i.e., an emulsion polymerisation in which a standard surfactant was also

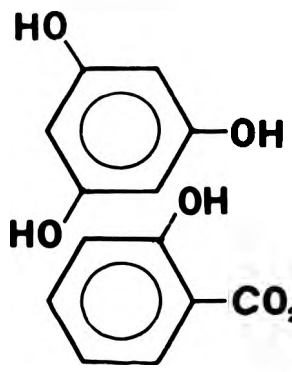
present;

(3) surfactant-free emulsion polymerisation of styrene.

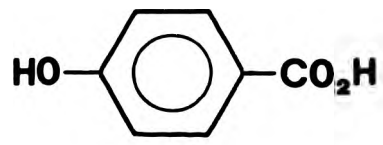
It was proposed that, when the results of the above programme were available, suitable compounds would be selected for more detailed study of their behaviour as initiators for emulsion polymerisation. This more detailed study would include investigation of the kinetics of emulsion polymerisation of styrene, where the selected compounds would be used as initiators/stabilisers in the absence of added surfactant.

1.7. Summary of the alcohols and amines used in preparing the esters and amides of 4,4'-azobis-4-cyanopentanoic acid. Below is a list of these alcohols and amines.

ethanol	C_2H_5OH
nonanol	$C_9H_{19}OH$
decanol	$C_{10}H_{21}OH$
undecanol	$C_{11}H_{23}OH$
hexadecanol	$C_{16}H_{33}OH$
octadecanol	$C_{18}H_{37}OH$
ethylene glycol	$HOCH_2CH_2OH$
trimethylol propane	$CH_3CH_2C(CH_2OH)_3$
pentaerythritol	$HOCH_2CH_2C(CH_2OH)_3$
cyclohexanol	
phenol	
resorcinol	

phloroglucinol 

o-benzoic acid



p-benzoic acid

decylamine $C_{10}H_{21}NH_2$

dodecylamine $C_{12}H_{25}NH_2$

tetradecylamine $C_{14}H_{29}NH_2$

decylammonium salt $C_{10}H_{21}N^{+}H_3\ ^{-}O_2C$---

ricinoleic acid

$CH_3(CH_2)_5CH(OH)CH_2CH{=}CH(CH_2)_2CO_2H$

11-hydroxyundecanoic acid $HO(CH_2)_{10}CO_2H$

fatty-alcohol ethoxylates $C_{17}H_{33}(OC_2H_4)_nOH$
where n = 2, 4, 6, 10, 14, 24, 30, 45, 60

1.8. Outline of the progress of the investigation. All the esters enumerated in the previous section and all the amides have been synthesised using 4,4'-azobis-4-cyanopentanoyl chloride and the appropriate alcohol or amine. However, the synthesis of the amide acids could not be accomplished. The synthesis, like those of the esters, had to be carried out at room temperature, because the azo group in 4,4'-azobis-4-cyanopentanoic acid decomposes slowly at room temperature and rapidly at higher temperatures[19]. Furthermore, the amino acids are soluble in water and glacial acetic acid only. Because acid chlorides of high molecular weight react very slowly with water, amide acids of high molecular weight have been synthesised from aqueous solution[123]. Nevertheless, the application of this method in this particular case did not yield the desired product. Solid-phase reaction too was attempted, but without success.

All the compounds synthesised were used in the emulsion polymerisation of styrene (i) in bulk polymerisation, (ii) in the presence of a conventional surfactant and (iii) in the absence of added surfactant. Chapter Five

describes the synthesis of the compounds and gives the results of the polymerisation experiments and the conclusions drawn from them. The nonyl, decyl, undecyl and hexadecyl esters behave as stabilisers, giving very monodisperse latices. Although the esters varied considerably in their capacity to act as stabilisers, all the compounds synthesised at this stage behaved as initiators for emulsion polymerisation in the presence of a surfactant, and almost all of the esters initiated bulk polymerisation.

However, after the completion of this preliminary investigation, the time came to choose suitable compounds for detailed study of their properties. It was then found that, although the straight-chain esters for more than a year had been yielding monodisperse latices in the absence of conventional surfactants, they now failed to produce latices. Furthermore, no polymerisation took place at all. The problem appeared to lie in repeating the preparation of the acid chloride. Chapter Five deals with the attempts which were made to synthesise the original compounds again. This was never achieved. As a consequence, the original programme had to be modified. These modifications are summarised below.

1.9. Objectives and plan of the present investigation. Using this second type of acid chloride, a second range of esters was prepared. The esters derived from the "Texofor A" series of ethoxylates were the only type of ester synthesised that yielded stable latices when used in the polymerisation of styrene in the absence of added conventional surfactant.

The first step was the synthesis of the esters of a range of "Texofor A" ethoxylates which varied in respect of the average number of ethylene oxide units per mole of hydrophobe base in the ethoxylate. The average number of ethylene oxide units per molecule varied from two to sixty. A preliminary study was carried out to establish the effectiveness of these compounds as initiators for emulsion polymerisation in the absence of added conventional surfactants. The most suitable examples were chosen for more detailed study of their behaviour. In particular, a study was made of the kinetics of the emulsion polymerisation of styrene initiated by these compounds in the absence of added conventional surfactant. The

intention was to study the effect of the following variables:

(1) The effect of temperature upon the rate of polymerisation;

(2) The effect of ester concentration upon the rate of polymerisation;

(3) The effect of phase ratio upon the rate of polymerisation;

(4) The stability of the latices produced;

(5) The molecular weight of the polymer produced;

(6) The particle size of the latex produced and its variation with time.

In addition, the rate of decomposition of the azo group in the ethoxylate esters was also studied. The effect of temperature upon the solubility of the ethoxylate esters in water was also investigated, since it is known that fatty-alcohol ethoxylates show the phenomenon of reverse solubility. Finally, surface tension experiments were carried out in order to determine the critical micelle concentration, if any, of the fatty-alcohol ethoxylates in water. It was hoped that the results of the above investigation would throw some light upon the mechanism of the kinetics of styrene emulsion polymerisation, where the initiator and the emulsifier are combined in the same molecule, and when no added conventional surfactant is present.

CHAPTER TWO

THEORIES OF EMULSION POLYMERISATION

2.1. Introduction. The early investigations into the possibility of emulsion polymerisation probably had their origin in the desire to synthesise materials analogous to natural rubber latex. Relatively little progress was made in the utilisation of emulsion polymerisation for several years following the initial discovery of the reaction at the beginning of this century. By the early 1930's, emulsion polymerisation had established itself as the preferred method of polymerisation in many cases, particularly for the preparation of synthetic rubbers.

Fikentscher is usually regarded as the first person to have realised that the principal locus of emulsion polymerisation reactions is not the monomer droplets but somewhere in the aqueous phase[21]. Harkins was the first to describe qualitatively a mechanism for emulsion polymerisation[22]. According to the Harkins theory, micelles containing solubilised monomer are the initial loci of polymerisation.

Smith and Ewart[23] then used the Harkins qualitative mechanism as the basis for their quantitative theory. The Smith-Ewart theory has two distinct aspects to it: (1) prediction of the number of particles formed by micellar nucleation, and (2) kinetics of free-radical polymerisation occurring within a large number of separate loci with the possibility of exchange of radicals between reaction loci and the external phase. Modifications and extensions of the general Smith-Ewart theory have been carried out by several workers[24-35], most of whom have accepted the basic concepts of the Smith-Ewart theory but have rejected some of the original assumptions.

Grancio and Williams[34,35] have claimed that the polymerising latex particle is not homogeneous, presumably because of restrictions on the diffusion of monomer to and within the particle. They therefore proposed a heterogeneous "core-shell" model for which a monomer concentration gradient exists within the particle. This proposal has been questioned by Napper[36] and by Gardon[37].

The view that particles are nucleated by a micellar mechanism, as postulated by Harkins and by Smith and Ewart has also been disputed. An alternative view is that the presence of micelles is not important as such for nucleation in emulsion polymerisation reactions. According to this view, the polymer particles are formed by the collapse of polymer molecules which have been formed by polymerisation in the aqueous phase. Priest[38], Roe[39] and Fitch[40-43] are the names associated with this mechanism of particle formation, which is known as "homogeneous nucleation".

Because of the complexity of emulsion polymerisation, it has proved impossible to construct an adequate general theory. The existing theories are not able successfully to account for many of the reported data.

2.2. The Harkins theory. The most important qualitative theory of emulsion polymerisation is that of Harkins[44], published in 1945. In this paper he proposed that the principal locus for the initiation of polymer particle nuclei was the soap micelles. In a second paper[45], the same author pointed out that new evidence had been found to show that the principal function of a monomer droplet was to act as a reservoir of monomer from which it diffuses through the water phase to the micelle.

In two subsequent papers[22,46], Harkins developed a theory for emulsion polymerisation. The main points are summarised below:

(1) In emulsion polymerisation using relatively water-insoluble monomers, e.g., styrene, all the polymer particle nuclei are initiated in the interior of the soap micelles.

(2) The monomer present in the micelle is insignificant in amount in comparison with the polymer produced. Therefore the monomer must diffuse from the monomer droplets to the micelles as polymerisation proceeds.

(3) A free-radical polymerisation mechanism is assumed.

(4) The function of the monomer droplets is to act as reservoirs of monomer.

(5) Very little polymer is formed in the water phase. The free radicals are produced in the water phase. They collide with other single molecules of this type much less frequently than with

micelles. Therefore, the slow rate of polymerisation in soap-free water as compared to that in micellar solutions is explained as being a consequence of the much smaller number of polymer particles present at any time in the soap-free system.

(6) Growth of the polymer-monomer particle leads to an increase in its surface area. It therefore tends to adsorb molecular emulsifier from the aqueous phase. This in turn leads to the dissociation of micelles containing monomer in which polymerisation has not started. Continual adsorption of micellar emulsifier onto growing polymer-monomer particles eventually leads to the disappearance of micellar emulsifier as such. This stage is reached relatively early in the reaction (approximately between 10 and 20% conversion). Also, the disappearance of the micelles is assumed to imply the cessation of particle nucleation.

(7) Continual diffusion of monomer into growing polymer-monomer particles eventually leads to the disappearance of the monomer droplets as a separate phase. This happens after the micellar emulsifier has disappeared. In consequence, the system now contains only monomer-swollen polymer particles dispersed in the aqueous phase.

It was the above qualitative theory developed by Harkins that served as a basis for the quantitative theory developed by Smith and Ewart.

2.3. The general Smith-Ewart theory. Smith and Ewart[23] gave the following quantitative treatment of polymerisation occurring in a large number of separate loci, exchange of radicals possibly occurring between the reaction loci and the external phase. Consider a system which consists of 1 cm^3 of dispersion medium (usually water), having suspended in it N number of actual or potential loci, each of which has a volume V and an interfacial area a. Suppose that free radicals are initiated only in the external medium. The rate of entrance of free radicals into a single locus will be

$$\frac{dn}{dt} = \frac{\rho'}{N} \qquad (2.1)$$

where ρ' is the overall rate of entrance of radicals into all the N loci, and n is the number of radicals in one locus. The rate of transfer out of a locus is written as

$$dn/dt = - k_o a (n/V) \qquad (2.2)$$

where k_o is the rate constant for the process, (n/V) is the concentration of free radicals in a locus, and a is the interfacial area through which transfer takes place. If destruction of free radicals takes place by mutual termination only, then the rate of destruction in a given locus is

$$dn/dt = - 2 k_t n [(n - 1)/V] \qquad (2.3)$$

The factor 2 arises because two free radicals are destroyed for each termination. In this equation, k_t is the rate constant for mutual termination, and (n - 1)/V is the concentration of free radicals with which any one of the n free radicals in a locus can react. Smith and Ewart derived the following steady-state equation for the number of loci containing various numbers of propagating radicals:

$$N_{n-1}(\rho'/N) + N_{n+1}k_o a[(n+1)/V] + N_{n+2}k_t[(n+2)(n+1)/V] = N_n\{(\rho'/N) + k_o a(n/V) + k_t n[(n-1)/V]\} \qquad (2.4)$$

This equation is derived on the assumption that, in the steady state, the rate of formation of reaction loci containing n free radicals is equal to the rate of disappearance of these loci.

Smith and Ewart considered the solution of these equations for three limiting cases:

Case 1, for which $n \ll 1$
Case 2, for which $n \simeq 0.5$
Case 3, for which $n \gg 1$

where n is the average number of free radicals in a polymer particle

Case 1 is applicable in situations where the rate at which radicals are transferred out of the loci by diffusion is great compared with the rate at which they are gained from the aqueous phase. Case 2 will apply if (a) there is no readily available mechanism by which the activity of the growing radical can be transferred out of the polymerisation locus, and (b) mutual termination of a propagating centre occurs almost instantaneously when a second radical is acquired by the locus. Case 3 will occur if

radicals enter the loci much more rapidly than they are destroyed by mutual termination. The rate law obtained for reaction systems conforming to Case 3 is exactly equivalent to that observed with reactions taking place in the oil phase and hence does not depend upon the size of the reaction loci. The results obtained for the emulsion polymerisation of styrene are best explained by assuming conformity to Case 2, where the number of free radicals per reaction locus is approximately 0.5. According to Smith and Ewart, the features of Case 2 explain the extraordinarily high rates of polymerisation and high molecular weights which are obtainable by emulsion polymerisation. The fundamental equation for the overall rate of polymerisation is remarkably simple, since it involves only the rate of polymerisation of a free radical and the number of reaction loci present. The rate of polymerisation during Interval II for reaction systems conforming to Case 2 is given by

$$R_p = \tfrac{1}{2} k_p[M] N \qquad (2.5)$$

where R_p is the rate of polymerisation, k_p is the rate coefficient for the propagation reaction, [M] is the monomer concentration in the particles, and N is the number of particles in a unit volume of the reaction system.

In order to find the total number of particles formed by micellar nucleation, Smith and Ewart considered how effective a given interfacial area is in collecting radicals from the dispersion medium. If the ordinary laws of diffusion hold, then the number of radicals entering a particle will be proportional to the radius of the particle. Hence the number entering a given area will be inversely proportional to the radius of the particle. This makes the problem rather complicated. However, the problem can be solved by considering separately two idealised situations, one of which should give too many particles and the other of which should give too few particles. Rather surprisingly, the two results are not greatly different. The actual situation lies somewhere in between.

2.3.1. Case of too many particles. For the case of too many particles, it is assumed that the very small micelles capture **all** the free radicals generated in the external phase, as long as micelles are still present. This will give a greater number of particles than are actually formed. The

expression for the number of particles obtained is

$$N = 0.53\,(\rho/\mu)^{2/5}(a_s S)^{3/5} \qquad (2.6)$$

where ρ is the rate of formation of free radicals per unit volume, μ is the growth rate (dV/dt) of a single polymer particle, S is the total amount of emulsifier associated with a unit volume of aqueous phase, and a_s is the interfacial area occupied by a unit mass of emulsifier.

2.3.2. Case of too few particles. The other idealised situation is that in which it is assumed that a given interfacial area always has the same effectiveness in collecting free radicals regardless of the size of the particle on which it is situated. This will give too few particles, because a given area on a very small particle will be more effective than the same area on a larger particle. The expression obtained for the number of particles in this case is:

$$N = 0.37\,(\rho/\mu)^{2/5}(a_s S)^{3/5} \qquad (2.7)$$

This equation is identical with the equation derived for the case of too many particles, except for the constant. Thus the correct solution for the real situation is presumed to be:

$$N = k\,(\rho/\mu)^{2/5}(a_s S)^{3/5} \qquad (2.8)$$

where $0.37 < k < 0.53$.

2.3.3. Cases 1 and 3 of the Smith-Ewart theory.

2.3.3.1. Case 1. This case considers the consequences when the average number of radicals per particle (n) is very much less than unity. This situation will occur if the rate at which radicals are transferred out of loci by diffusion is great compared with the rate at which they are gained from the aqueous phase. Under such conditions, for termination of radicals taking place mainly in the aqueous phase, the rate of polymerisation is given by

$$R_p = k_p[M]V_p \alpha \sqrt{(\rho/2k_t)} \qquad (2.9)$$

where V_p is the total volume of dispersed polymer per unit volume of aqueous phase, and α, given by c_p/c_w, denotes the partition coefficient for radicals between particles and aqueous phase, where c_p and c_w are the average concentrations of free radicals in the polymer particles and in the water, respectively.

Alternatively, if the termination takes place in the polymer particles, the rate of polymerisation is given by:

$$R_p = k_p [M] \sqrt{(\rho V_p / 2k_o a)} \qquad (2.10)$$

In equation (2.5), the rate of polymerisation for reaction systems conforming to case 2 is directly proportional to N. However, for case 1 the situation is more complex. Equation (2.9) predicts first-order dependency of rate upon the total volume of the polymer particles, the rate being independent of the number of particles; equation (2.10) predicts that the rate of polymerisation is proportional to the square root of N.

2.3.3.2. Case 3. For this case, n, the average number of initiating radicals per reaction locus, is considerably greater than unity. This situation will occur if radicals enter the loci much more rapidly than they are destroyed by mutual termination. The overall rate of polymerisation per unit volume of aqueous phase for this case is given by:

$$R_p = k_p [M] \sqrt{(\rho V_p / 2k_t)} \qquad (2.11)$$

Under these conditions, the rate depends only upon the total volume of the polymer particles, and not upon the number of particles into which that volume is subdivided. The system is then effectively a suspension polymerisation in which the free radicals are supplied from the external phase.

2.3.4. Validity of the Smith-Ewart model. The Smith-Ewart theory is valid only for a limited number of cases[5]. The theoretical predictions of Case 2 have been confirmed for the emulsion polymerisation of styrene by some workers, while others have found significant variations. Vanderhoff[47] has concluded that the Smith-Ewart Case 2 is followed for particle diameters of 100-150 nm or smaller at lower rates of radical initiation (e.g., by the persulphate ion at 50°C or lower). At larger

particle sizes, or with greater rates of radical generation, the deviation becames significant. This model presumes a number of inherent conditions, and in order to get a more realistic model, corrections have to be made to compensate for the unreality of these assumptions.

The following are some conditions which are assumed as the basis of the Smith-Ewart model, and which are not necessarily met in practice:

(1) Polymerisation proceeds exclusively in the monomer-swollen micelles.

(2) The initiator is soluble only in the external phase, and its half-life is considerably greater than the duration of the reaction.

(3) Entry of a second initiating radical into a particle containing a propagating polymer chain results in instantaneous bimolecular termination.

(4) All particles are of identical size and grow at constant absolute rate, i.e., dv/dt is constant.

(5) A well-defined transition exists between nucleation and growth stages.

(6) Surfactant emulsifies the monomer efficiently, and is well adsorbed by the particles.

(7) Polymerisation loci are nucleated until all micellar surfactant has disappeared, and fresh particles are neither formed nor lost by coalescence after nucleation is complete.

(8) The monomer is a good solvent for the polymer and the growing particle is homogeneous.

2.4. The Gardon theory. A revised theory based on an extension of the assumptions first proposed by Smith and Ewart, and also by Haward, has been proposed by Gardon[48]. It differs from the earlier theories in that the relationships derived are strictly quantitative and contain no adjustable parameters. Also, the validity limits of the prediction are defined.

For very short reaction times, the variation of conversion with time in Interval I is predicted to be

$$P = 0.351\,(k_p/N_A)\,(d_m/d_p)\,\phi_m R t^2 \qquad (2.12)$$

where k_p is the rate coefficient of propagation, N_A is the Avogadro number, d_m and d_p are the densities of monomer and polymer respectively, ϕ_m is the volume fraction of monomer in the particle, R is the number of radicals produced per unit volume of water per unit time, and t is the time of reaction. Thus, while the particles are nucleating, the conversion is proportional to the initiator concentration and to the square of the time. The result obtained for the number of particles per unit volume, N, formed during Interval I is

$$N = 0.208\, A_I^{0.6}\, (R/K)^{0.4} \qquad (2.13)$$

where K is the rate of change of particle volume = $d(r^3)/dt$, and A_I is the polymer-water interfacial area. During Interval II, for Smith-Ewart Case 2 the rate of polymerisation is independent of conversion and is given by

$$R_p = 0.435\, (1 - \phi_m)\, (KA_I)^{0.6}\, R^{0.4} \qquad (2.14)$$

The rate of polymerisation is of the order of 0.6 with respect to the emulsifier concentration, and of the order 0.4 with respect to the emulsifier concentration. These orders were also predicted by the Smith-Ewart theory. The rate of termination is expressed in terms of n, the number of radicals per particle, as follows:

$$dn/dt = (R/N) - (k_t/VN_A)\, n\, (n - 1) \qquad (2.15)$$

In this equation, (R/N) is the average rate of entry of radicals into a given particle, V is the volume of the monomer-swollen particle, and k_t is the rate coefficient for the mutual termination of radicals. According to Gardon, since the particle volume increases with time, the termination rate decreases with time and so there is no steady-state as postulated by the Smith-Ewart theory. Furthermore, since, at constant rate of initiation, the termination rate decreases, n must increase with time and there should be no constant conversion rate in Interval II. The conversion-time relation is predicted to be:

$$R_p = At^2 + Bt \qquad (2.16)$$

On the basis of this non-steady state solution, the average number of radicals per particle is found to be:

$$n = 0.5\,[1 + (4A/B^2)\,R_p]^{0.5} \qquad (2.17)$$

The Gardon theory predicts that the distribution of radicals amongst particles broadens with increasing n or with increasing conversion. Since particle growth is proportional to n, this distribution also defines the distribution of growth rates. In principle, the particle-size distribution could be calculated from the growth-rate distribution. With increasing conversion, more and more particles will be found which grow much slower or much faster than the average, and therefore the particle-size distribution will broaden with increasing conversion. The Gardon theory also predicts that, with increasing conversion, the molecular weight should increase in Interval II, should reach a maximum at the onset of or during Interval III, and should subsequently decrease.

2.5. The Medvedev theory. The theory developed by Medvedev[24,49] attaches little importance to the number of particles initiated. Instead, it is the adsorbed emulsifier layer which is regarded as the principal locus for particle initiation. Thus, the most important parameter is the total surface area stabilised by adsorbed emulsifier. The polymerisation rate is not affected by the transition of emulsifier from the micelles to the surface of the monomer-polymer particles. If the amount of emulsifier is insufficient for stabilisation after the disappearance of micelles, then the polymer particles agglomerate to a limited extent, thus reducing the total surface area. Medvedev developed kinetic expressions for the cases in which the initiator is either water-soluble or oil-soluble.

For the case of water-soluble initiators, he distinguished between the cases in which the primary radicals are formed in the aqueous phase or in the adsorbed emulsifier layer. Medvedev derived the following equation for the rate of disappearance of monomer:

$$-d[M]/dt = k_p\,[M] \left(\frac{2k_d k_1}{k_t(k_2+k_d)}\right)^{\frac{1}{2}} [I]^{\frac{1}{2}}\,[S] \qquad (2.18)$$

where k_p denotes the rate of polymerisation, [M] the monomer

concentration in the monomer-polymer particles, and [S] the surfactant concentration. k_d is the rate of production of radicals from the adsorbed initiator molecules; k_1 is the rate of transition of the initiator molecules from the external phase to the adsorbed phase; k_t is the rate of termination of two growing polymer chains, and k_2 is the rate at which initiator molecules transfer from the adsorbed phase to the external phase. [I] is the total initiator concentration.

In the case of an oil-soluble initiator, the difference lies in the fact that the initiator does not pass into the adsorption layer from the aqueous phase but from the bulk of the polymer particles. The concentration of monomer and initiator in the adsorption layer will, to a first approximation, be equal to, or at least proportional to, the concentration within the polymer particles.

2.6. The core-shell model. A modified model for emulsion polymerisation reactions was proposed by Grancio and Williams[34,35]. The basic idea of this theory is that a monomer-swollen polymer particle is not homogeneous. They propose that a particle comprises a polymer-rich core with relatively little monomer, and a shell which is rich in monomer. This theory was proposed in order to explain certain results for the kinetics of the emulsion polymerisation of styrene. In particular, the monomer-polymer ratio in the particles was found to decrease with conversion in their experiments. In this "core-shell" model, the outer shell is the major locus of polymerisation, whilst virtually no polymerisation occurs in the core because of its monomer-starved condition. A Smith-Ewart "on-off" mechanism necessarily prevails within the monomer-rich shell. According to this theory, a changing overall monomer-polymer ratio in the particles is consistent with constant rate of polymerisation within the particle because reaction takes place in an essentially pure monomer environment.

Napper[49] has pointed out that the requirements of the "core-shell" model, as given by Grancio and Williams, conflict with the "ordinary" laws of diffusion. He argues that, if polymerisation occurs primarily in the peripheral zones of the particles, any diffusion approach predicts that these outer regions would, if anything, be monomer-deficient in any dynamic situation, because of the consumption of monomer therein.

According to Napper, the inner region would function as a monomer reservoir, the chemical potential of the monomer decreasing in the outward direction. Gardon[50] has also reconsidered the question of the existence or otherwise of monomer concentration gradients in polymerising latex particles. He concludes that there are unlikely to exist within the growing particles any concentration gradients of sufficient magnitude to affect the kinetics of the reaction.

2.7. Developments of the Smith-Ewart theory. The steady-state distribution of free radicals amongst the emulsion particles, described in the form of a recursion formula by Smith and Ewart, has been solved only for limiting cases. Stockmayer[25] has put forward a general solution which may be useful in the treatment of emulsion particles of intermediate size. His result can be best expressed by the following equations:

$$Z = \frac{n}{a/4} = \frac{I_0(a)}{I_1(a)} \qquad (2.19)$$

where Z is a factor expressing the degree of subdivision of the reaction mixture into small particles, $a = 4(R_i/2k_t)^{\frac{1}{2}}N_A v$ and N_A is the Avogadro number, v is the volume of the particle, n is the average number of radicals per particle, I_o and I_1 are the Bessel functions of the first kind of zero and first order respectively. The radical concentration, defined as moles of radicals per litre, is given by:

$$[R\cdot] = n\,N/N_A \qquad (2.20)$$

and the overall rate of polymerisation is given by:

$$R_p = Z\,(R_i k_p^{\,2}/2k_t)^{\frac{1}{2}}[M] \qquad (2.21)$$

Equations (2.20) and (2.21) were derived by Vanderhoff[51]. They are general, and are therefore applicable to solution, bulk, suspension and emulsion polymerisation systems. Also, Stockmayer gives a formula for the distribution of locus populations. The breadth of the distribution shows that for large particles the distribution becomes very narrow.

In emulsion and suspension polymerisation, the reaction mixture is subdivided into a large number of small particles. O'Toole[28] has

attempted to predict the stationary distribution of growing molecules in a latex particle resulting from a zero-order absorption from the aqueous phase, a first-order desorption or chain-stopping transfer, and a second-order termination reaction. He has also considered the case of initiation within particles.

Experimental studies show that exit of free radicals from the particles can play a significant role in determining the rate of polymerisation, and also in determining the properties of the latex produced. In addition, reentry and/or aqueous-phase termination of these exited radicals may also occur. Unfortunately, the Stockmayer-O'Toole solution is difficult to evaluate if the exit rate coefficient is zero. Their method is inapplicable if reentry and/or aqueous-phase termination of exited free radicals occurs.

Ugelstad and Hansen[52] have proposed a continued-fraction method for calculating the Bessel function ratio that is required for determining the average number of radicals per particle. Unfortunately, their method does not yield the number distribution of particles containing n free radicals. Ballard et al[53] have recently derived a new solution of the general Smith-Ewart equation by assuming that entry into a reaction locus containing n free radicals causes instantaneous bimolecular termination, leaving (n - 1) free radicals. Ballard et al have derived the following equation in the steady state:

$$N_n = [\rho + (n+1)k + n(n+1)c]N_{n+1} - (n+2)kN_{n+2} - (n+3)(n+2)cN_{n+3} \qquad (2.22)$$

where N_n = the number of particles containing n radicals;
ρ = the rate coefficient for radical entry;
n = the number of radicals per polymer particle;
k = the rate coefficient for radical exit;
c = the rate coefficient for bimolecular termination.

An approximate value of n is required in order to initiate the computation:

$$dn/dt = \rho - k\bar{n} - 2c\bar{n}^2 \qquad (2.23)$$

The above equation has also been used by Birtwistle and Blackley[54]. This technique is extended to include reentry and aqueous-phase termination.

$$\rho = \rho_n + \alpha k\bar{n} \qquad (2.24)$$

where ρ = the rate coefficient for the entry of radicals,

ρ_n = the rate coefficient for the entry of free radicals generated by the initiator,

α is a parameter describing the fate of exited free radicals, and

$\alpha k\bar{n}$ = the rate coefficient for reentry of exited free radicals.

The above equation has been extended to cover the case where aqueous-phase termination may also take place.

The case where $\bar{n} << 1$ has been extensively studied by Gilbert and Napper[55]. These workers consider the behaviour of the system in the non-steady state. It seems that for vinyl chloride and vinyl acetate desorption of free-radicals from the particles may be especially significant. They derive analytical solutions for one set of differential equations that describe some types of emulsion polymerisation where the average number of radicals per particle is much smaller than unity without using the steady-state approximation. To predict the rate of polymerisation, they calculate n by a method that involves the solution of large numbers of simultaneous differential equations of the Smith-Ewart type, modified because of the non-steady state. One term allows for the entry of free radicals into the particles. They are able to solve the equation if they ignore the last term. This seems a reasonable assumption if $k_{ex} >> k$, either as a consequence of very rapid transfer of free-radical activity from the particle or because the polymerisation has an abnormally low termination constant. Gilbert and Napper found that the attainment of a steady state at longer times for $\bar{n} << 1$ implies that the common assumption that a linear experimental plot of per cent conversion against time necessarily corresponds to $\bar{n} = 0.5$ is incorrect. From the equations they solved using matrices, they plotted conversion against time and obtained a linear plot up to 50% conversion. At higher conversions, the polymerisation becomes diffusion-controlled and their theory no longer applies. From the slope of the conversion/time curves they were

able to find ρ , the rate of entry of oligomeric free radicals into the particle. They found that only one radical in 2.6×10^3 of those produced in the aqueous phase actually enters the particles for vinyl acetate. This may be associated with the high water solubility of that monomer. This would entail many monomer additions in the aqueous phase before oligomers with suitable surface-active properties were produced. Apparently the small values of n observed in this system result not only from rapid exit of free radical activity from the particle but also from a very small capture efficiency.

In a second paper, these workers[56] extended the range of n values covered by their matrix method by including bimolecular termination. At this stage, solutions of the set of differential equations that allow both for free-radical exit from the particles and for bimolecular termination have not been achieved. However, solutions are given for the case where bimolecular termination in the particles is included but radical exit is assumed to be negligible. The assumptions are very similar to those which enable Smith and Ewart to solve their Case 2; however, Gilbert and Napper's solution describes the entire course of polymerisation, not just the steady state that may ultimately be achieved. These assumptions are thought to be applicable to the emulsion polymerisation of styrene.
Weiss and Dishon[57] point out that the analysis given by Gilbert and Napper is complicated. An exact solution is not given, and so Weiss and Dishon maintain that the perturbative generalisation of Gilbert and Napper's work shows considerable complications. Weiss and Dishon, using a generating function, provide a simpler derivation of an exact solution to Gilbert and Napper's equation that allows so-called "perturbation corrections" to be easily derived.

In a further paper[58], the Napper group of workers present essentially time-dependent solutions valid for systems in which the mechanisms of free-radical exit, entry and termination are permitted to operate simultaneously. The only restriction on the general non-steady-state solutions presented is that the rate of entry of free radicals into the particles must be less than the rates of exit and and/or bimolecular termination. The analytical solution provides a complete description of the entire course of polymerisation, not merely of the steady state that is

eventually attained. As a result, it becomes possible to explore the way in which exit and termination reactions influence the time taken to reach the steady state. Using matrix calculus, they obtained the following results:

$$P/A = w \lambda^{-1} [\lambda t + \exp(-\lambda t) - 1] \qquad (2.25)$$

where P is the per cent conversion, A is a constant of proportionality, t is the time of reaction,

$$\lambda = [k(k + 2c) + 4\rho c] / (k + 2c) \qquad (2.26)$$

and

$$w = \frac{2\rho[k^2 + k(3c + \rho) + 2c^2 + 3\rho c]}{2k^3 + k^2(6c + 2\rho) + k(4c^2 + 10\rho c + \rho^2) + 8\rho c^2 + 4\rho c^2} \qquad (2.27)$$

where ρ is the rate coefficient for entry of free radicals into the particles;

k is the rate coefficient for the exit of free radicals from the particles;

and c is the rate coefficient for bimolecular termination within the particles.

When $\rho \ll k$, the exit term dictates the value of $\bar{n}$ and we have a first-order dependence of $\bar{n}$ on ρ. As ρ increases, i.e., as the rate of entrance increases, it eventually dominates the exit term, and a zero-order dependence on ρ is obtained as termination tends to dictate the value of $\bar{n}$. The solutions derived also permit the analysis of reactions which go to completion without ever reaching the steady state.

Birtwistle and Blackley[59] give an explicit analytic solution for the number of reaction loci per unit volume containing n radicals as a function of time t, for reaction systems in which the following conditions are fulfilled:

(1) Radicals enter the reaction loci at constant rate;

(2) The loss of radical activity from the reaction loci is first-order with respect to the concentration of the radicals in the loci;

(3) No lost radicals re-enter the loci;

(4) The volume of the reaction loci is constant;

(5) No new loci form or are destroyed.

The general expression obtained is:

$$n_n(t) = \frac{N}{n!} \left(\frac{\rho}{k}(1 - e^{-kt})\right) \exp -\frac{\rho}{k}(1 - e^{-kt}) \qquad (2.28)$$

where N is the total number of reaction loci,

ρ is the average rate of entry of radicals into a single locus,

and k is the rate coefficient for the loss of radical by a first-order process.

The above result is obtained by first deriving the following result for the locus-population generating function:

$$\psi(\xi,t) = N \exp \frac{\rho}{k}(\xi - 1)(1 - e^{-kt}) \qquad (2.29)$$

where ξ is an auxiliary variable.

The above results have been generalised to include cases in which the parameters ρ and k, which characterise the rates of entry and exit of radicals respectively, are time-dependent.[60]

Gilbert and Napper[61] criticised the above solution because the procedure does not include the treatment of a decay process in the presence of a small thermally-induced contribution to the rate of background thermal entry that is required for these studies. The Australian group[62] provide equations for the growth of the particles in an emulsion polymerisation reaction in which the mechanism of free-radical entry, exit and termination operate, and where particle growth also occurs. This predicts the full volume distribution at any time, and provides scope for a more comprehensive comparison between theory and experiment.

An even more complete treatment has been given by Brooks[63]. He considers the re-adsorption of desorbed radicals and the decay of the radical generators as well as the processes previously considered. Brooks shows that failure to include re-adsorption of desorbed radicals may lead

to serious error in the estimation of radical population.

An analysis of the behaviour of emulsion polymerisation systems relaxing from a given state when the radical source is removed has been carried out by Birtwistle and Blackley[64]. These workers have applied their general solution to obtain predictions for the decay of the reaction from three types of distribution of locus polymerisation:

(1) a distribution of the Stockmayer-O'Toole type;

(2) a Poisson distribution;

(3) a homogeneous distribution.

Their results have been summarised by Blackley[65]. These papers include numerical predictions for the set of equations in the most general form. Birtwistle and Blackley have made an approximation to the Smith-Ewart equations and obtained a solution that gives a Poissonian distribution of locus population, i.e., the number of particles that contain a given number of radicals.

The Napper group[66] have put forward a mathematical formulation which describes the evolution of the number distribution of the molecular weight of linear polymer chains that grow in the course of emulsion polymerisation. The resulting set of coupled ordinary differential equations takes into account the microscopic events of free-radical entry, exit, chain annihilation, bimolecular termination (by combination and by disproportionation) and chain transfer in a mono- or polydisperse system.

Very similar values for the rate coefficients for the first-order loss and thermally-initiated entry processes were obtained by two independent procedures. The first[61] allowed the relaxation kinetics, whereas the second measured the approach to a chemically-initiated steady state[67]. The result showed that, for a styrene emulsion polymerisation, the average number of free radicals per particle in the steady state may have values significantly less than 0.5 at lower initiation concentrations. This appears to be a consequence of a first-order free radical loss process. The rate coefficient for this process was found to be inversely proportional to the square of the swollen radius. The dependence of the entry rate coefficient upon the initiator concentration suggests that radical capture was relatively inefficient. These workers claim that the

efficiency of radical capture increases with decreasing initiator concentration. They have also detected the existence of a background initiation process that causes polymerisation to proceed in the absence of added initiator. This appears to be the emulsion polymerisation analogue to the thermally-induced bulk polymerisation of styrene. Very closely related work has been presented by Brooks and Makanjuola[68]. In the work of Hawkett et al[67], monomer droplets were present throughout the polymerisation. Consequently the particle volume would not be constant, but would increase with time. They claim that the radical-capture efficiency was very low. This is not surprising, since they used Gardon's formula to calculate the rate of radical production. Unfortunately, the assumptions in this formula are (1) that radical desorption is absent, (2) that all radicals generated in the aqueous phase are absorbed by the particles, and (3) that n is equal to 0.5 in the constant-rate period. The result was unusually high rates of radical production, which would result in capture efficiencies which were artificially low.

Brooks and Makanjuola[68] have found that the values of the desorption coefficient k_o were not affected greatly by the monomer concentration in the particles, nor by the degree of surface saturation of the growing particles by the surfactant.

2.8. Kinetics of emulsion polymerisation in Interval III. On reaching Interval III, the monomer concentration in the polymer particles diminishes, since in this period there are no more monomer droplets to feed the polymer particles[69]. First-order kinetics with respect to monomer concentration in the particles would be expected, but the rate coefficient for termination may fall to such an extent with the increasing viscosity of the particles that a gel effect may be observed[70]. The rate of termination is dependent upon the viscosity of the medium. The result of decreased rate of termination is increased rate of polymerisation and increased molecular weight. This phenomenon is called the "gel effect" or "Trommsdorff effect". In emulsion polymerisation systems, where the polymer concentration at the site of reaction is generally high, the gel effect is particularly important[51]. This effect can decrease the magnitude of k_t by an order of magnitude[5]. If the monomer-polymer mixture becomes a glass during polymerisation, the mobility of even the

monomer can be severely restricted. In such cases, the rate of polymerisation may decrease to near zero before polymerisation is complete, and complete conversion may not be possible within reasonable time limits without increasing the temperature. Usually it is necessary to increase the temperature to above the glass transition temperature (T_g) of the polymer-monomer mixture.

Relatively little attention has been paid to the kinetics of Interval III, largely because of the difficulty associated with a quantitative prediction of the variation in k_t. The rate of termination decreases, and hence so does the value of α, since $\alpha = v \rho_A/(Nk_t)$, where ρ_A is the rate of absorption of radical oligomeric chains in the polymer particle and v is the average volume of a particle.

Friis and Hamielec[71] have made use of the results of kinetic measurements on bulk polymerisation. From such results they find k_t for methyl methacrylate. They have also applied the same method to vinyl acetate[72,73]. They have further studied the gel effect in the emulsion polymerisation of other vinyl monomers[74].

Friis and Hamielec[75] have also studied the polymerisation of styrene. They assume m = 0, where $m = k_o a/k_t$, a is the average area of a particle, and k_o is the specific rate constant for the escape of radicals from the particle. As shown by Smith-Ewart-O'Toole, these conditions lead to the value of 0.5 for $\bar{n}$ when α is small compared with unity; i.e., when k_t is large. On the basis of kinetic experiments on the thermal polymerisation of styrene, Hie and Hamielec[76] developed the following empirical equation:

$$k_t = (k_t)_o \exp [-2 (Bx + Cx^2 + Dx^3)] \qquad (2.30)$$

where B, C and D are constants and $(k_t)_o$ is the termination rate constant in pure styrene, and x is the degree of conversion.

Harris et al[77] have put forward a kinetic model for the Interval III emulsion polymerisation of styrene. The experimental evaluation was carried out using monodisperse latex particles of known particle size with a determination of instantaneous rates using an adiabatic calorimeter as

reactor. In this way, they were able to determine the variation in k_t and k_p with conversion for latex particles having a diameter of 40 nm. The average number of radicals per particle was 0.5. This permitted a direct measure of the decrease of the propagation constant with conversion. A glass transition occurs at approximately the T_g of the polymer-monomer mixture; i.e., when the monomer-polymer ratio has fallen to the point where the T_g of the polymer-monomer mixture equals the polymerisation temperature, the glass transition occurs. At this stage the unreacted monomer acts as a plasticiser. Harris et al give equations from which the limiting conversion (x_e) can be estimated. Their model takes account of diffusion-controlled termination and propagation reactions.

Ugelstad and Hansen[52] have assumed that the amount of monomer in the aqueous phase may be neglected. They consider how n, and therefore the rate of polymerisation, changes in Interval III. They further assume that k_t is constant up to very high conversions, and that the rate of chain transfer, k_f, is also constant.

Hawkett et al[67] have used seeded emulsion polymerisation systems to obtain values for the rate coefficients that covered the entry of free radicals into, and the exit of free radicals from, the latex particles in Interval III. In addition, the dependence of the bimolecular termination rate coefficient k_t, upon the ratio of monomer to polymer in the particle could be determined.

2.9. Theory of homogeneous nucleation. In many theories of emulsion polymerisation, the main locus of particle initiation has been considered to be the monomer-swollen micelles. One of the assumptions of the above theories is that, from the beginning of Interval II, where all the surfactant is either (1) stabilising the growing polymer particles, (2) helping to stabilise the monomer droplets or (3) dissolved in the water, the number of latex particles should remain constant. Since zero-order kinetics are observed during this period (i.e., the rate is independent of the concentration), the monomer concentration in the polymer particles must remain constant. However, it has been shown by Robb[78] that the number of latex particles is not constant during Interval II of the emulsion polymerisation of styrene, but increases, although the rate of

polymerisation is constant. He concludes that new particles must have been created during the period of constant rate.

Further doubts concerning the importance of surfactant micelles for particle nucleation arise from the observation that aqueous solutions of monomers such as methyl methacrylate, vinyl acetate, acrylonitrile and even styrene can be emulsion polymerised in the absence of surfactant. Thus the presence of micelles is not essential for the formation of polymer particles.

The idea that particles can be formed by the polymerisation of monomer molecules dissolved in the dispersion medium was first proposed by Priest[38]. Later Roe[39] proposed a theory of particle initiation based on Priest's ideas: In Roe's theory, particle generation in a polymerising emulsion is pictured as resulting from interaction of a free radical and a monomer molecule both of which are dissolved in the aqueous phase. A monomer radical thus initiated is assumed to react with additional dissolved monomer molecules to become a growing polymer chain suspended in the aqueous phase. Continued development of this sort causes the growing chain to assume the aspect of a polymer radical stabilised against flocculation by adsorbed emulsifier and swollen with adsorbed monomer. Alternatively, at any stage in its history prior to adsorption of an adequate protective layer of emulsifier, the growing radical may be swept up by a pre-existing polymer particle, or by a swollen emulsifier micelle, provided micelles are present. A particle nucleus may be said to have identity as a polymer particle when further growth takes place only by chain propagation and combination within its own structure and when flocculation with other molecules or agglomerates of similar size is excluded. In Roe's theory, the generation of particle nuclei persists at a rate which depends on the concentration of monomer and free radicals but not on other constitutive variables. Achievement of permanent identity as polymer particles by nuclei depends on the availability of emulsifier. Particle formation by this mechanism is known as "homogeneous nucleation".

Basically, the hypothesis is that oligomeric chains are formed in solution in the dispersion medium by polymerisation of dissolved monomer. These oligomers grow by free-radical propagation until at some critical chain

length the dissolved oligomers achieve a high degree of "supersaturation". They then form a new polymer phase by collapse of the chains upon themselves, thereby forming primary polymer particles. Monomer is absorbed into these primary particles, and under most conditions these primary particles become the chief loci for the subsequent emulsion polymerisation[79]. In the case of surfactant-free emulsion polymerisation, the stability of the latex particles is believed to be achieved by ionic end-groups derived from the initiator (in many cases - SO_4^- derived from persulphate ions). Fitch and coworkers[41] have developed a quantitative theory for calculating the number of particles which are formed by this type of mechanism. It requires a knowledge of the rate of effective radical generation and the average distance a primary oligomeric radical diffuses in solution before it "self-nucleates". The oligomeric radicals can either (1) grow to the critical size and then precipitate (homogeneous nucleation), or (2) be captured by pre-existing particles. As particle formation continues, the probability of capture by pre-existing particles increases until ultimately all oligomers are captured. Thereafter no new particles form, and particle nucleation ceases. In a second paper, Fitch et al[42] have described the isolation and characterisation of soluble oligomers which are believed to correspond to the growing chain radicals which are present in the aqueous phase, both prior to the formation of any particles as well as throughout the reaction after particles are formed[42]. In the absence of stabiliser and of charged end groups, the particles which form by homogeneous reaction are unstable and flocculate. In the absence of added stabiliser, but with stabilising end groups present, a large number of primary particles are formed many of which subsequently undergo extensive flocculation. Thus three competitive processes are involved, namely, radical generation, radical capture by existing particles, and particle flocculation. The rates of these processes are denoted by R_i, R_c and R_f, respectively. The rate of particle formation is then presumed to be given by:

$$dN/dt = R_i - R_c - R_f \qquad (2.31)$$

During the earliest stages of particle nucleation, no particles are present, so that every radical generated produces a primary particle.

Therefore under these conditions the rate of particle formation will be given by $dN/dt = R_i$, where N is the number of particles per unit volume and t is the time. Later, as particles become formed, they will capture some of the oligomeric radicals formed in solution. As capture of the oligomeric radicals becomes important, the rate of particle nucleation will be correspondingly reduced. The rate of particle formation will then be given by:

$$dN/dt = R_i - R_c \qquad (2.32)$$

When Fitch and Tsai first put forward a quantitative model for homogeneous nucleation, the effect of diffusion was not taken into consideration. It was Hansen and Ugelstad[80], as well as La Mer[81], who demonstrated the need for a diffusion-controlled mechanism.

As N increases, the rate of capture will approach the rate of radical generation, until finally a steady state is reached when dN/dt is zero. The final number of particles, N, is then given by

$$N = \int_0^{t_s} (R_i - R_c)\, dt \qquad (2.33)$$

where t_s is the time required to reach the steady state for which $R_i = R_c$. The rate of capture, R_c, is diffusion-controlled and is given by

$$R_c = 4\pi \bar{D}_{op} C_s N_{rp} \qquad (2.34)$$

where D_{op} is the average diffusion coefficient, which is determined by the relative motions of oligomeric radicals and polymer particles, and C_s is the steady-state concentration of oligomeric radicals. C_s is given by

$$C_s = R_i / (4\pi \bar{D}_{op} N_{rp} + 2D_o/L^2) \qquad (2.35)$$

In this equation, $\bar{D}_o$ is the average diffusion coefficient for the growing oligomeric free radicals, and L is given by

$$L = (2\bar{D}_o DP_{max}/k_p[M])^{\frac{1}{2}} \qquad (2.36)$$

DP_{max} is the maximum degree of polymerisation which is attained by the oligomeric radicals before they collapse, k_p is the rate constant for propagation, and [M] is the monomer concentration in the aqueous phase. Qualitatively, as L increases, R_c approaches R_i, thereby reducing the rate of nucleation, dN/dt. Although the rate of capture is diffusion-controlled, it may or may not be reduced by electrostatic repulsion between the oligomeric radicals and the polymer particles. Whether or not this happens depends upon such factors as the size of the particles, their surface electrical potential, ψ_o, and the ionic strength of the dispersion medium.

If the primary particles formed are colloidally stable, they will be produced in great numbers in a short time, after which R_c rapidly approaches R_i and dN/dt falls essentially to zero. A steady state is reached when no new particles are formed. The time-dependence of N will be as indicated in curve A of Fig. 2.1.

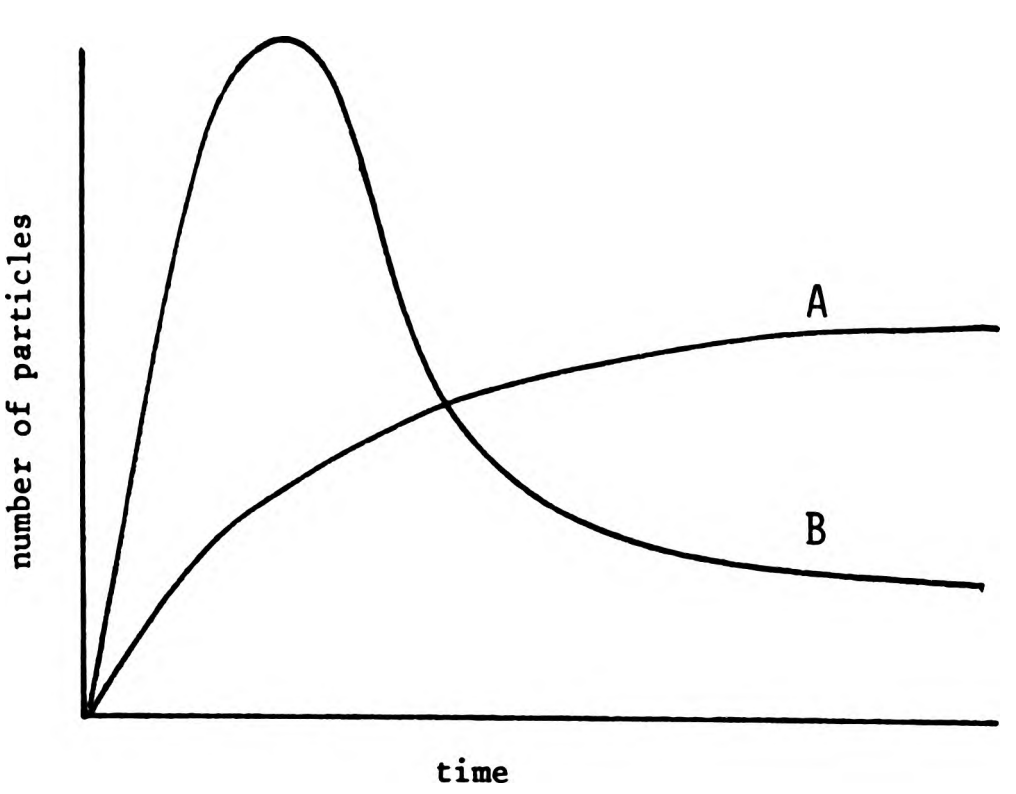


Fig. 2.1: Variation in number of particles in (A) absence of flocculation and (B) presence of flocculation.

Usually, however, the primary particles are colloidally unstable and flocculate to a limited extent. For systems where electrostatic repulsions are involved, flocculation will occur until a critical surface potential, ψ_c, is developed which effectively prevents further flocculation. When flocculation occurs, the rate of flocculation is denoted by R_f. It is supposed that, in the flocculation process, when two particles collide they adhere to each other and subsequently fuse or coalesce to form a single particle in which most, if not all, of the surface groups which were present on the original particles become situated at the surface of the new particle. The consequent reduction in surface:volume ratio leads to an increase in the surface charge density and hence in the surface electrical potential, ψ_o. This in turn produces a rapid reduction in the rate of flocculation as the process continues. Under these conditions, the variation in number of particles with time will be as shown by curve B of Fig. 2.1. When flocculation of primary particles occurs, the rate of particle formation is given by equation 2.34. The rate of flocculation is given by[82]

$$R_f = -dN/dt = k'N^2 \qquad (2.37)$$

where $k' = 4D_pH/W$. In this latter equation, D_p is the diffusion coefficient of the particles, H is the collision distance, usually taken as twice the radius of the particles, and W is the Fuchs stability factor. W depends upon the total density of electric charge which is fixed at the particle surface due to end groups and adsorbed surfactant molecules, as well as upon the ionic strength of the medium.

Fitch[43] has attempted to make experimental estimates of R_c. He concludes that the collision theory gives a reasonable estimate for the capture rate, but that the mechanism of capture of radicals by particles is diffusion-controlled. Comparison of the calculated absolute values for R_c with experimental values based upon the diffusion theory indicates

(a) that there is an interaction between particles and oligomer radicals, and

(b) that diffusion of radicals <u>out</u> of particles may in some cases occur.

Hansen and Ugelstad[83] have given a more rigorous theoretical treatment of the theory of homogeneous nucleation. The physical factors which influence the capture rate of oligomers in particles are discussed, including the possibility of desorption of radicals once adsorbed. Quantitative expressions for electrostatic repulsion and for reversible diffusion of radicals are derived. The result shows that the particle number goes through a maximum, and that simultaneous nucleation and flocculation of primary particles can take place after Interval I is complete.

CHAPTER THREE

THEORY OF STABILITY OF LYOPHOBIC COLLOIDS

3.1. Definition of a lyophobic colloid. The formation of stable latices is a primary objective of this project. Because polymer latices are examples of lyophobic colloids, it is important to understand the factors which affect the stability of lyophobic colloids, and the theories which have been proposed to explain the effects of these factors. Colloids are multi-component systems in which the dispersed phase is in a state of subdivision in the dispersion medium such that at least one dimension is in the range between approximately 10 nm and 1000 nm[84,89]. Colloids are generally classified as lyophobic (i.e., possessing no affinity for their dispersion medium) or lyophilic (i.e., possessing affinity for the dispersion medium). Thus, the simplest lyophobic colloids are essentially two-phase systems, which consist of a disperse phase and a dispersion medium, the two phases being such that there is no thermodynamic tendency for them to mix. Polymer latices are examples of lyophobic colloids.

3.2. Stability of lyophobic colloids. Lyophobic colloids have associated with them a large area-to-volume ratio of the disperse phase (i.e., the area of interface between disperse phase and dispersion medium is large in relation to the volume of disperse phase) and hence have high interfacial energy. They are thermodynamically unstable. The term "stability" as applied to lyophobic colloids is generally understood to mean the ability of the colloidal dispersion to persist in an altered state of colloidal dispersion. It is the interplay of the various attractive and repulsive forces between the particles that determines the stability behaviour of lyophobic colloids. There are six possible basic interparticle forces which operate in a colloidal system[90,91]:

(a) Electrostatic repulsive forces: These arise from the presence of a surface potential ψ_o, and the consequent space-charge cloud in the dispersion medium.

(b) Van der Waals attractive forces: These arise from the presence of electrical dissymmetry in the atoms and molecules which make up the particles.

(c) Steric repulsive forces: The presence of adsorbed

macromolecules on the particle surfaces gives rise to this type of force.

(d) Solvation repulsive forces: These arise from the removal, displacement or rearrangement of solvent molecules in the interfacial regions.

(e) Born forces: These are very short-range repulsive forces.

(f) Depletion forces: These arise from the exclusion of polymer molecules from between colloid particles.

There are at least four possible mechanisms by which stability can be imparted. Each of these deperds upon the nature of the repulsive interparticle forces which are operative. The stabilising mechanisms are:

(a) electrostatic stabilisation;

(b) steric stabilisation;

(c) hydration stabilisation;

(d) depletion stabilisation.

3.3. Electrostatic stabilisation of lyophobic colloids; the DLVO theory. The DLVO theory (the name is derived from the initials of the workers who developed the theory, namely, Deryagin, Landow, Verway and Overbeek)[84] considers electrostatic stabilisation to be the cause of the stability of lyophobic colloids. The DLVO theory views the stability of colloids as arising from the presence of bound electrical charges at the particle surfaces, and from consequent electrical repulsions between the particles. Opposing these repulsions are attractive forces of the van der Waals type. If the repulsion forces can be reduced sufficiently so that the van der Waals attraction becomes dominant, then particles colliding with each other will stick together to form more-or-less permanent aggregates.

3.3.1. Electrostatic repulsion. The basic cause of the electrostatic stabilisation of any colloidal system is the acquisition of electrical charges at the surface of the particles. In the case of latex systems, the particle surface can acquire an electrostatic charge by either one or both of the following mechanisms:

(i) ionisation of chemical groups at the ends of polymer chains on the surface of the particle, and

(ii) adsorption of surfactant ions from the dispersion medium at the particle surface.

As a result of the balance between electrostatic and diffusional forces, the ions in the region between the charged particle surface and the bulk solution are distributed in what is known as a "diffuse electrical double layer". This diffuse double layer has no sharply-defined end-point but gradually approaches the composition of the dispersion medium as one moves away from the surface.

In 1905 Helmholtz[92] proposed that the double layer consists of two layers of opposite charge, analogous to a parallel-plate electrical condenser, a distance d apart. One of the layers is formed by a positive charge on the surface, the other consisting of an equivalent number of counterions located in a single plane adjacent to the charged surface. The remainder of the system is unaffected by the presence of the double layer. Because the double layer as a whole is electrically neutral, and the layer of counterions screens the charge completely, the surface potential ψ_0 drops linearly to zero. This approach neglects any tendency for the layer of counterions to disperse under the influence of thermal motion.

Gouy[93] and Chapman[94] modified Helmholtz's model by taking into account the thermal motion of the ions in the solution, which prevents the counterions from becoming arranged in a compact manner. The thermal motion of ions is counteracted by the electrostatic forces. The overall effect of these opposing forces is to produce a diffuse space-charge cloud in the interfacial region. According to the Gouy-Chapman model, the structure of the double layer is determined by their valency. This predicts a high concentration of counterions near the charged surface for high electrolyte concentration and/or high electrical potential. This defect arises from neglect of the finite dimensions of the ions.

In 1920 Stern[95] modified the Gouy-Chapman theory by introducing two corrections.

(i) The first correction allowed for the finite dimensions of the ions in the layer immediately adjacent to the surface.

(ii) The second made allowance for the possibility of specific adsorption of the ions at the surface.

The above two corrections facilitate the formation of a compact layer of thickness δ on the charged surface by certain counterions. However, these corrections do not apply to the ions which are situated beyond the compact layer, so that these ions form a diffuse double layer. The compact layer is called the "Stern layer". The Stern region of the double layer is a region within which the counterions are permanently attached to the particle surface by strong electrostatic forces. ψ_d is known as the Stern potential. Outside the Stern plane may be found a hydration layer of water molecules, and these too are firmly attached to the particle and move with it during its Brownian motion. This outside boundary of the particle is called the plane of shear. The electrical potential at the plane of shear is called the zeta potential (ζ). Fig. 3.0 gives a diagrammatic representation of the process.

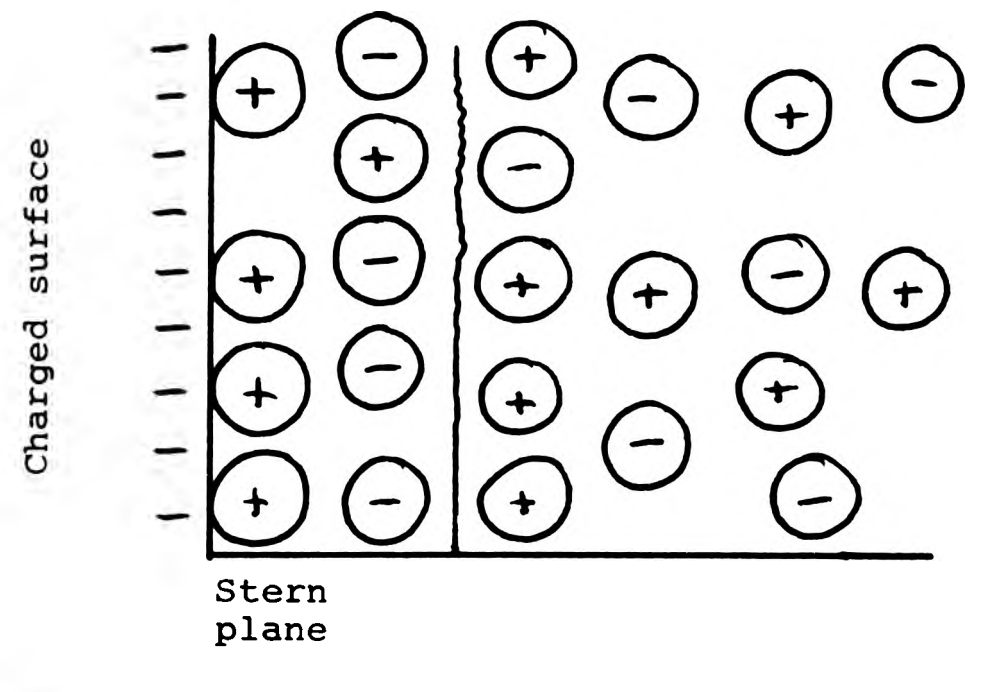


Fig. 3.0: Diagrammatic representation of the electrical double layer associated with a planar surface.

Unlike the surface and Stern potentials, zeta potentials can be measured experimentally. The exact relationship between the zeta potential and the surface potential or the Stern potential is not known.

The thickness of the double layer is given by $1/K$, where, for a symmetrical electrolyte present in the dispersion medium, K is given by

$$K = (8\pi n z^2 \epsilon^2 / DkT)^{\frac{1}{2}} \qquad (3.1)$$

In this equation, n is the number of ionised groups in the bulk solution, z is the valency of the ions, ϵ is the electronic charge, D is the dielectric constant of the medium, k is the Boltzmann constant, and T is the absolute temperature. The double layer thickness is an inverse function of both the concentration and the valency of the counterions. The ionic concentrations and ionic valencies can be combined together to give a quantity known as the ionic strength of the medium. Ionic strength, μ, is defined as

$$\mu = \tfrac{1}{2}\sum c_i z_i^2 \qquad (3.2)$$

where the summation covers all types of ions in a given solution.

When two particles, each carrying a diffuse double layer, approach each other, the diffuse counterion atmospheres begin to overlap each other. The result is that work must be performed to bring particles together. The repulsive energy, V_R, at a given inter-particle distance, is the work which must be performed to bring the particle to that point from infinite separation. Approximate expression for V_R are given by Ottewill[96]. For surface potentials less than 50 mV:

$$V_R = \tfrac{1}{2}\epsilon a \psi_0^2 \ln[1 + \exp(-KH_0)] \qquad (3.3)$$

where a is the particle radius, and H_0 is the minimum distance of separation between the particles. In general, for a given latex system, V_R is a function of the quantity KH_0, and it decays exponentially with increasing distance of separation between particle surfaces.

3.3.2. Van der Waals attraction. In the absence of any repulsive interparticle forces between the particles of a dispersion, it is well known that the dispersion undergoes rapid coagulation[97]. This behaviour is a consequence of long-range forces of attraction operative between the particles. These forces increase with decreasing interparticle distance. They are known as van der Waals attractive forces.

To be able to compete with the electrostatic repulsion forces, the attractive force must be of comparable magnitude and range of action. The van der Waals force between particles can be calculated as the summation of the London dispersion forces between all pairs of atoms in the two particles. The origin of these dispersion forces lies in the charge-fluctuation in an atom associated with the motion of electrons. A phase difference in the fluctuating dipoles leads to mutual attraction. The approximate expression derived for the attractive energy, V_A, between two particles each of radius a, at a distance of separation H_o, for $a >> H_o$ is

$$V_A = -Aa/12H_o \qquad (3.4)$$

where A is the so-called Hamaker constant. The Hamaker constant characterises the attraction between the particles and the dispersion medium. This expression for V_A is not valid at distances of separation between particles larger than about 10 nm. At such distances, allowance must be made for the retardation effect. The retardation effect is caused by the finite time necessary for an electromagnetic wave to travel from one atom to the other atom in which it is inducing a dipole.

3.3.3. Total energy of interaction between two particles. According to the DLVO theory, the total energy of interaction, V_T, between two particles of an electrostatically stabilised lyophobic colloid is given by the sum of the attraction and repulsion energies; i.e.,

$$V_T = V_A + V_R \qquad (3.5)$$

Fig. 3.1. shows the general nature of the variation of V_T with the inter-particle distance, H_o. At very short distances, a deep potential-energy

minimum, usually known as the primary minimum, occurs as a consequnce of strong attractions between the particles. At large distances, the energy associated with electrical repulsions falls off more rapidly with increasing distance of separation than does that associated with the van der Waals attraction. The consequence is a secondary minimum, V_s [99].

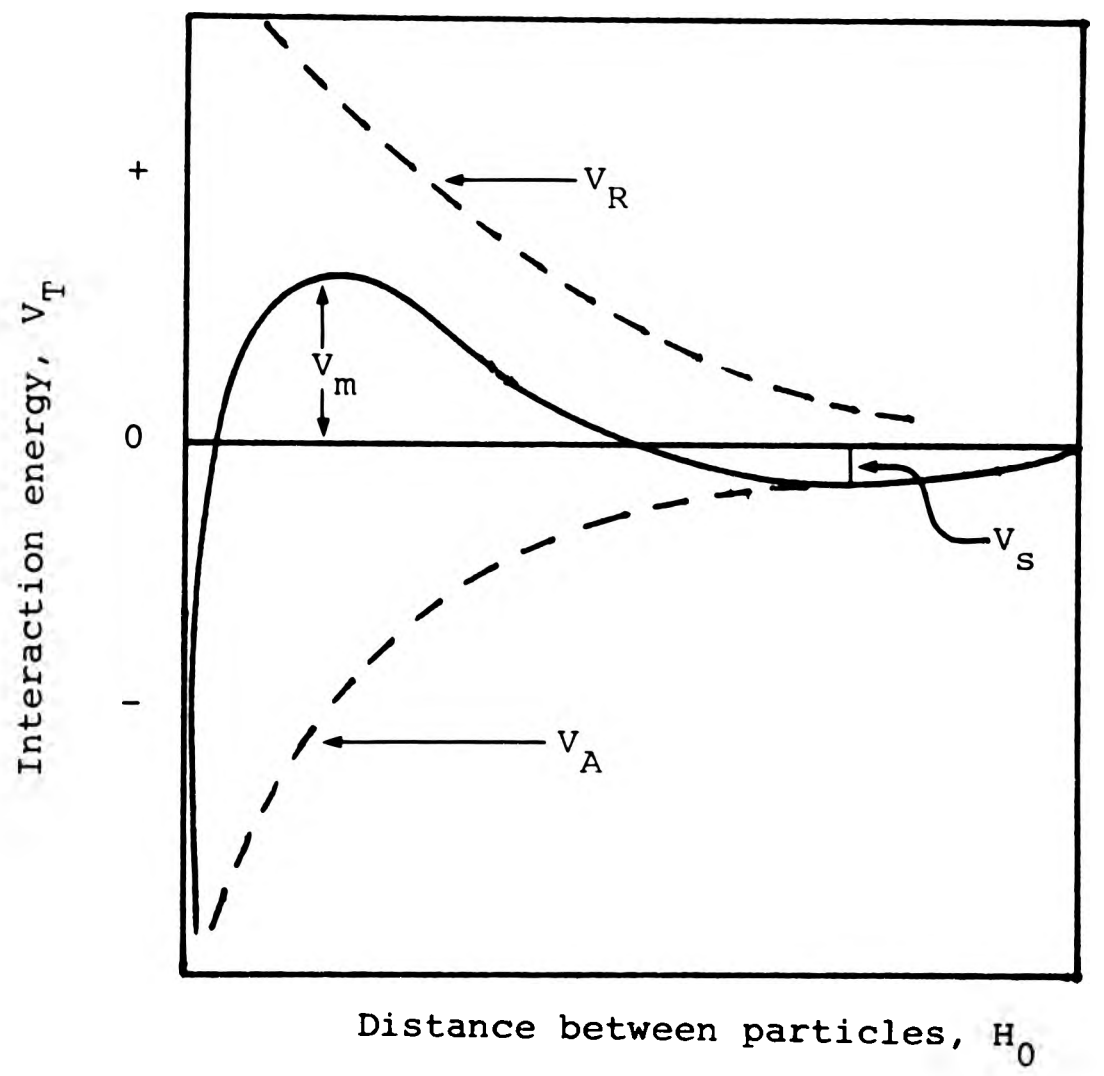


Fig. 3.1: Potential energy curves for two particles of a lyophobic colloid as a function of the inter-particle separation, H_0.

The stability of a lyophobic colloid is dependent upon the height of the potential energy barrier, V_m. The potential energy barrier must be surmounted if the particles are to approach one another sufficiently closely to enter the deep primary minimum, thus causing irreversible coagulation. The value of V_m necessary to prevent this is considered to be approximately 10-20 kT. This corresponds tc an electrical potential of about 50 mV. The colloid is then considered to be kinetically stable. Aggregation in the secondary minimum is not usually observed with small

particles, because the energy reduction will be comparable to the mean thermal energy. Aggregation is therefore easily reversed by Brownian motion[98].

In 1917 Smoluchowski[97] analysed the kinetics of the coagulation process. The findings showed that the rate of disappearance of primary particles in the initial stages of coagulation could be written as:

$$-dN/dt = kN_o^2 \qquad (3.6)$$

where N_o is the number of particles per unit volume initially present and k is the rate constant. For rapid coagulation $k = k_o = 8\pi DR$, where D is the diffusion coefficient of a single particle and R is the collision radius. Fuchs[100] showed that if diffusion in the presence of an energy barrier is considered, i.e., slow coagulation, then k can be put equal to k_o/W, where W is the stability ratio. Thus,

$$-dN/dt = (k_o/W)N_o^2 \qquad (3.7)$$

The usefulness of Equation 3.7 lies in the fact that the rate of coagulation in the early stages can be determined experimentally. Thus, values of k and W in the slow coagulation can be obtained.

It was pointed out by Fuchs[100] that the factor W is related to V_T through the equation

$$W = 2a\int_o^\infty \exp(V_T/kT)\, dh/(h + 2a)^2 \qquad (3.8)$$

where a is the particle radius and h is the distance of separation between particles.

As a further development Reerink and Overbeek[101] showed that the gradient of the curve obtained when log W is plotted against log C_e could be given as

$$(d \log W)/(d \log C_e) = -2.06 \times 10^7 (a\gamma^2/v^2) \qquad (3.9)$$

Here C_e is the electrolyte concentration, v is the valency of the counterion, and γ is said to be $[(\exp(ve\psi_e/2kT) - 1)/(\exp(ve\psi_e/2kT) + 1]$. It is not clearly established whether ψ_e should be taken as the Stern potential or as the zeta potential. Equation 3.9 can be subjected to direct experimental tests.

The van der Waals attractive forces are not easily varied. The repulsion energy, on the other hand, can be modified by changing the surface potential on the particles, or the valency of the electrolyte in bulk solution, or the concentration of electrolyte. Consequently, the stability of latices in many technological applications is controlled by the magnitude of the electrostatic repulsion.

3.4. Steric stabilisation of lyophobic colloids. Stability may also be imparted to a lyophobic colloid by adsorbed non-ionic surfactants and macromolecules which provide a steric barrier. Such barriers prevent the particles from approaching one another closely enough for the van der Waals forces to be sufficient for aggregation to occur.

The stabilising effect of non-ionic macromolecules was first observed by van der Waarden[102] during studies on the stabilisation of carbon black dispersions in hydrocarbon media. These studies showed that alkylated aromatic molecules stabilised these dispersions, and that the stabilising effect increased with the length of the alkyl chain and with the number of chains per molecule. It was suggested that the highly-polarisible aromatic nuclei anchored the stabilising molecule, whilst the alkyl chains projected into the dispersion medium and prevented close approach of the particles.

Heller and Pugh[103] appear to have been the first to use the term "steric stabilisation" to denote the stabilisation of uncharged colloidal particles against coagulation by adsorption of non-ionic polymer molecules. However, Napper[107] has pointed out that the term "steric" is used in this context with a broad thermodynamic connotation, rather than with the restricted meaning used in organic chemistry.

The term "steric stabilisation" is now used to describe all the different stabilising mechanisms which arise from the presence of uncharged

adsorbed macromolecules. Steric stabilisation is effective in both aqueous and non-aqueous media. Several reviews of steric stabilisation have been published[104-106].

3.4.1. Characteristic features of steric stabilisers. For steric stabilisation to occur, the surfactant or polymer should be adsorbed on or chemically combined with the surface of the lyophobic colloid. It is essential that these stabilisers extend an appreciable distance into the dispersion medium, and that at the same time they be firmly anchored to the particle surface. The extended portions projecting from the surfaces provide a steric barrier which stabilises the dispersion. The anchor groups function efficiently if they are insoluble in the dispersion medium and prevent the stabilising units from moving away from the interaction zone on the approach of a second particle.

In the case of polymers, the conformation of the adsorbed molecule on the surface of the particle is an important factor which determines the efficiency of stabilisation. The theories of polymer adsorption assume that the structure of a polymer can be represented as a flexible chain of segments, some of which are in direct contact with the surface, whilst others extend into the dispersion medium. A diagrammatic representation is given in Fig. 3.2.

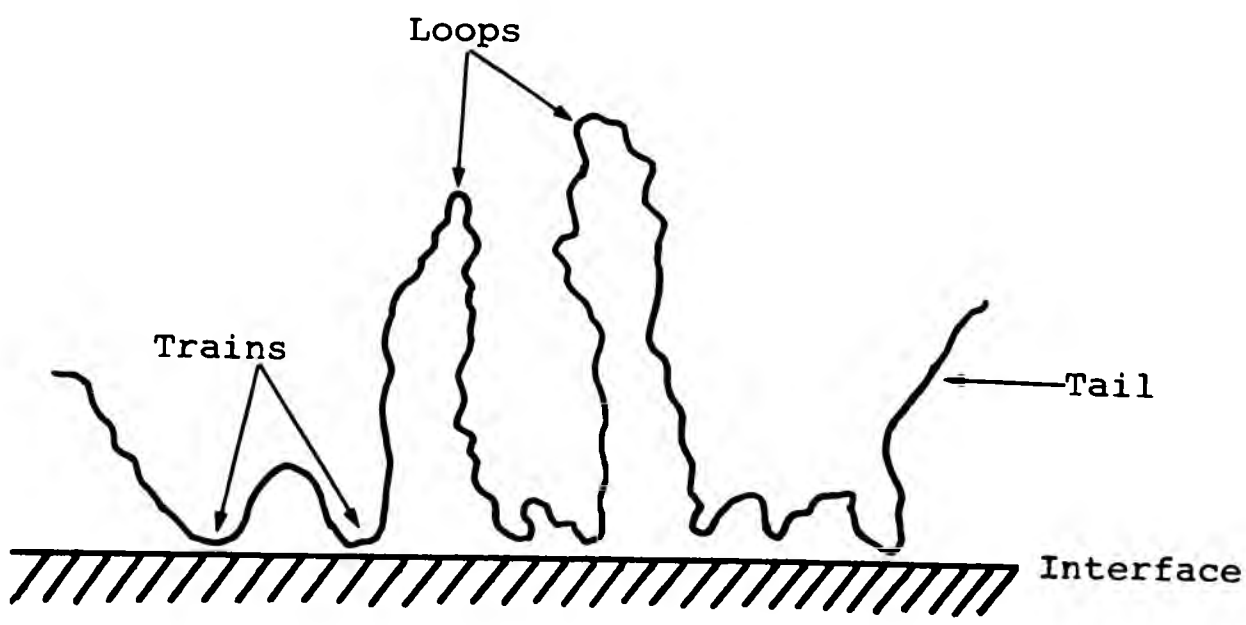


Fig. 3.2: Schematic representation of an adsorbed polymer molecule on the surface of a particle.

Those segments that are in direct contact with the surface are referred to as "trains" and those in between and extending into the dispersion medium as "loops". The free ends of the adsorbed polymer which extend into the dispersion medium are known as "tails". The stabilising effect is due to the loops and the tails.

Polymer adsorption can be characterised by means of three important parameters:

(i) the amount of adsorption per unit area;

(ii) the fraction of segments in contact with the surface;

(iii) the segment density distribution in the vicinity of the surface, this being important for stabilisation.

These factors in turn depend upon a number of variables, such as the nature of the adsorbed polymer, the adsorbant, the solvent, the temperature, and also the concentration and the molecular weight of the adsorbed molecule[104]. The adsorbed polymer may not always confer stability. Colloid stability can be either increased or decreased by adsorbed polymer[108].

3.4.2. Principles of steric stabilisation. The steric repulsive forces and interaction energies that occur when the adsorbed nonionic polymer chains of adjacent particles interact originate from two possible causes:

(1) If the distance of separation of two particles is less than twice the thickness of the adsorption layer, then mixing of the two adsorption layers takes place. If this process is accompanied by a net increase in the free energy, repulsion occurs between the particles. Such a mechanism is very probable when the concentration of the polymer in the adsorption layer is low. This mechanism was first proposed by Fisher[109]; it is referred to as the "mixing" mechanism[110]. It has also been referred to as an "osmotic effect"[111].

(2) When the polymer concentration in the adsorption layer is high, the particles undergo pseudo-elastic collisions on approach rather than mixing. The polymer molecules adsorbed on the particle lose configurational entropy. This mechanism was first proposed by Jackel[112]. It is referred to as the "denting" mechanism[110] or

"volume restriction effect"[111].

The effectiveness of steric stabilisation can be predicted by considering the balance of the attractive van der Waals forces and the steric repulsive forces of two particles on close approach. The total potential energy of interaction for sterically-stabilised particles, V_S, is given by

$$V_S = V_{SR} + V_A \qquad (3.10)$$

where V_{SR} and V_A are the steric repulsive and attractive potential energies respectively.

Steric repulsion is best characterised by the change in Gibbs free energy, ΔG_S, of the particles on close approach. The second law of thermodynamics implies that a positive value of ΔG_S is necessary for repulsion if the temperature and pressure are kept constant. Steric repulsive forces are of shorter range than the electrostatic and van der Waals forces; the forces increase very rapidly with decrease in interparticle distance. Ottewill and Walker[112] have shown theoretically that the free energy of interaction, ΔG_S, arising from the interactions between two spherical particles of radius a depends upon the following factors:

(i) the concentration of nonionic stabiliser in the adsorbed layer;

(ii) the thickness of the adsorbed layer:

(iii) the distance between the particle surfaces;

(iv) an enthalpic term which characterises the interaction of the stabilising group with the solvent, and

(v) an entropy of mixing term for the stabilising layer.

On the close approach of two sterically-stabilised colloidal particles, there is a change in Gibbs free energy. This is given by

$$\Delta G_S = \Delta H - T\Delta S \qquad (3.11)$$

where ΔH and ΔS are the enthalpy and entropy changes respectively. ΔG_S must be suitably positive for stability to be observed[113-115]. The following are the circumstances which will lead to a positive ΔG_S:

(a) Both ΔH and ΔS are negative, and $- T\Delta S$ is greater than $-\Delta H$.

The effect of the entropy term opposes flocculation and outweighs the effect of the enthalpy term. This is known as "entropy stabilisation". If, with decreasing temperature, the entropy contribution is reduced to a certain value such that the enthalpy and entropy terms become equal, then flocculation will proceed rapidly. Thus entropically stabilised dispersions are generally characterised by the occurrence of a flocculation process on cooling.

(b) ΔG_S can be positive for positive values of ΔH and ΔS, provided that ΔH exceeds $T\Delta S$. In this case, the enthalpic effect promotes stabilisation and the entropic effect promotes flocculation. The term "enthalpic stabilisation" is used to describe this circumstance. On heating, $T\Delta S$ should normally increase more rapidly than ΔH and hence flocculation will occur.

(c) ΔG_S will be always positive for a situation having a positive ΔH and a negative ΔS. Both enthalpic and entropic effects promote stabilisation in this case. This mechanism is referred to as "enthalpic-entropic stabilisation". In this case, flocculation will not occur at any temperature.

The generic term "steric stabilisation" thus encompasses entropic, enthalpic and enthalpic-entropic stabilisations. The enthalpic effects are probably more important in the stabilisation of aqueous dispersions, whereas the entropic contributions are more important in the stabilisation of non-aqueous systems[116,117].

Fig. 3.3 shows a schematic plot of steric repulsive potential energy versus the interparticle distance H_o. V_S rises rapidly with decrease of H_o.

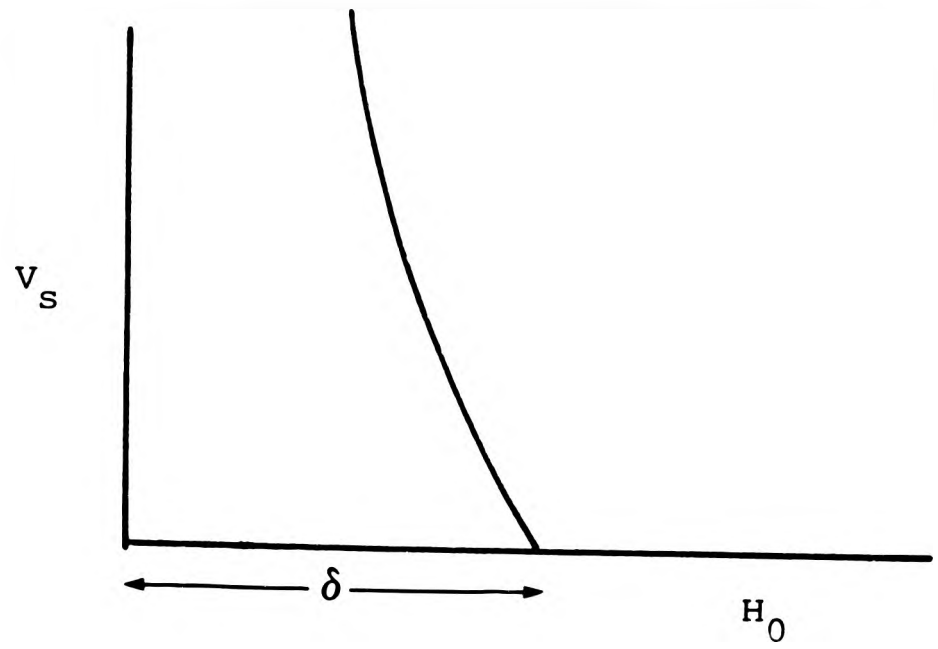


Fig. 3.3: Schematic representation of the variation in steric repulsive potential energy, V_S, with the distance of surface separation, H_0, for two spheres sterically stabilised by adsorbed layers of thickness $\delta/2$.

Fig. 3.4 shows a plot of potential energy versus interparticle separation for sterically-stabilised particles. The potential energy curve does not exhibit the deep primary minimum and the primary maximum, which are the important features of the potential energy curve for electrostatically-stabilised particles. This is because of the presence of the adsorbed layer. As the steric repulsion vanishes at twice the thickness of the adsorbed layer, attraction predominates at intermediate and large distances. This gives rise to a minimum in the curve. The depth of the minimum, V_{min}, in the potential energy curve determines the stability of the system. If V_{min} is greater than 5kT, the particles are irreversibly flocculated. If V_{min} has a value in the range between kT and 5kT, the particles aggregate reversibly and can be redispersed.

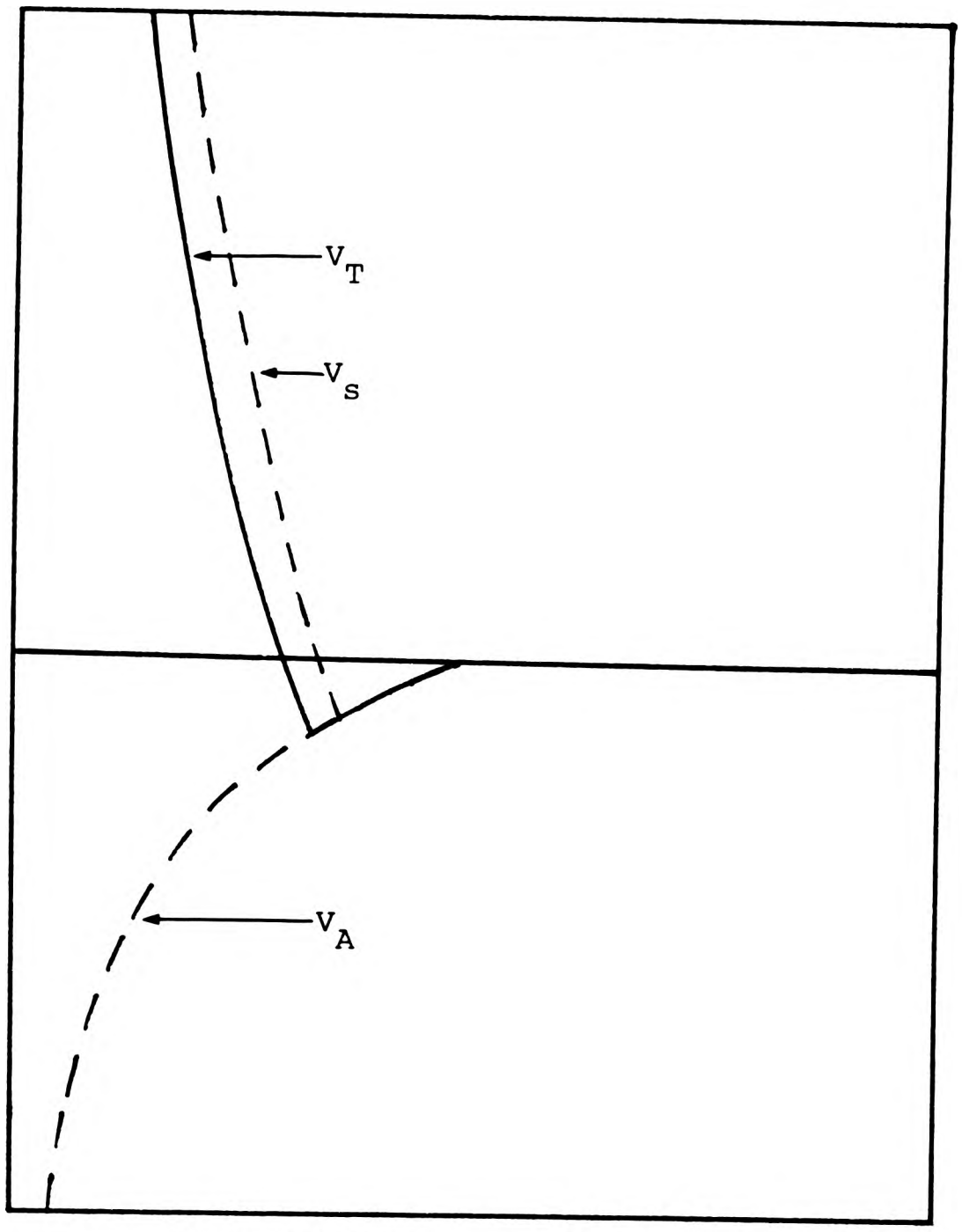


Fig. 3.4: Schematic representation of a potential energy curve for two particles of a sterically stabilised lyophobic colloid.

Although the above is a summary of the basic thermodynamic conditions which lead to steric stabilisation, detailed conclusions cannot be drawn by consideration of the above factors alone. The dispersion medium and the interaction of the polymer segments with the dispersion medium should also be considered. Also, the quality of the solvent for the stabilising

chain is an important factor which controls the stability of sterically-stabilised lyophobic colloids.

The potential energy curve for two particles in a lyophobic colloid which is both sterically and electrostatically stabilised[114] is illustrated schematically in Fig. 3.5. This case is of particular interest, since many steric stabilisers for aqueous lyophobic colloids are ionised -- e.g., proteins, alginates, sodium carboxymethylcellulose, etc. It is clear that entry into the deep primary minimum is prevented by the steric barrier. The steric repulsion confers stability upon the system, even though the electrical double layer has been considerably compressed.

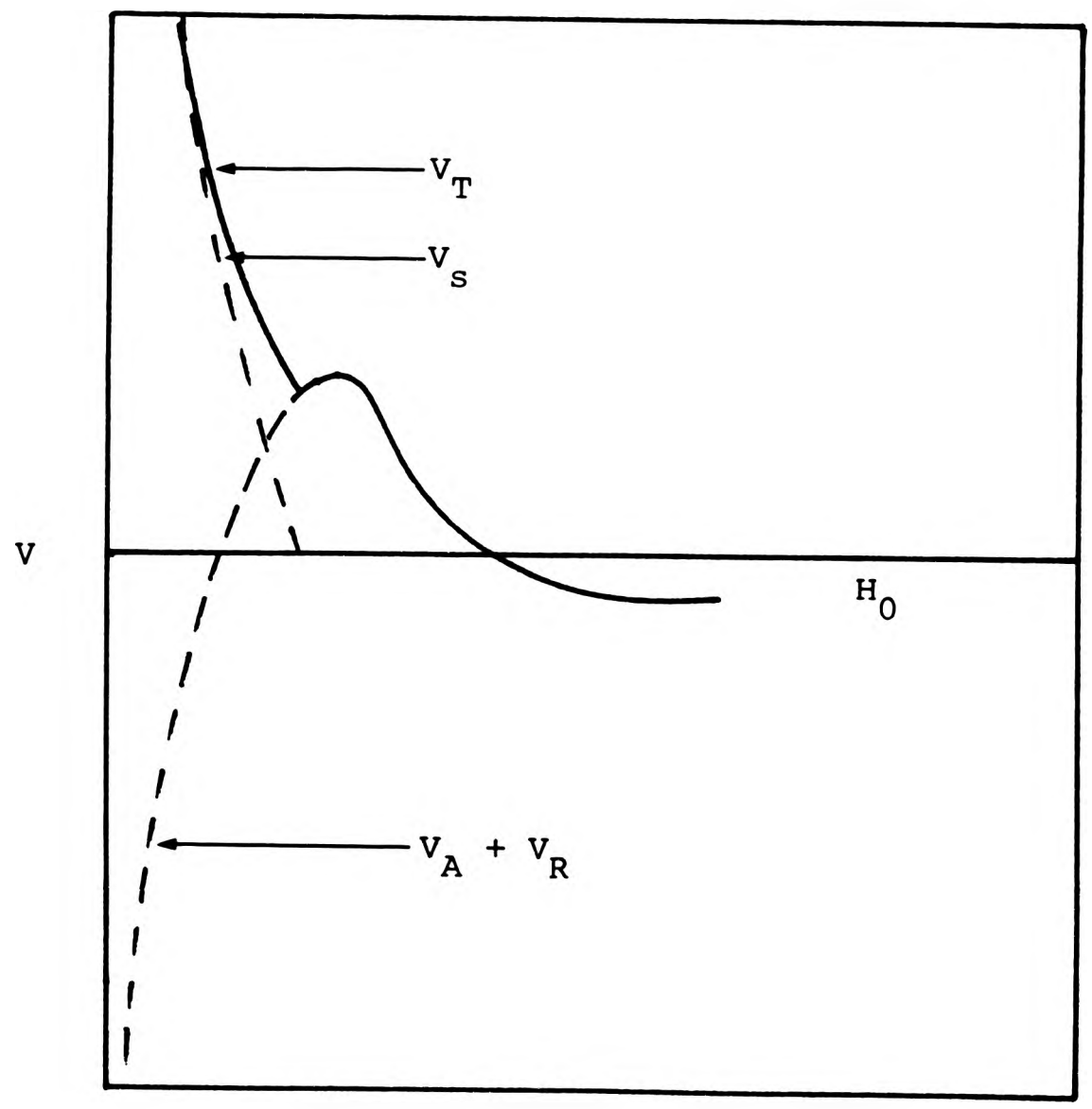


Fig. 3.5: Schematic representation of potential energy curve for two particles in a lyophobic colloid which is both sterically and electrostatically stabilised.

In general, the addition of nonionic surfactants improves the stability of electrostatically-stabilised lyophobic colloids.

A discussion of the strengths and weaknesses of the theory of electrostatic stabilisation, as well as steric stabilisation, has been given by Overbeek[118]. Some of the limitations of the theory of electrostatic stabilisation are as follows:

(1) The repulsion equation is based on the theory of the electrical double layer. In this theory, the ions can be treated as point charges. This treatment is not correct, since it predicts that the counterions can reach impossibly high concentrations near the surface.

(2) A further serious consequence of the Stern-Goüy model is the fact that, under coagulation conditions, the potential at the Stern plane is neither high nor independent of the concentration and the charge number of the ions.

(3) Although the surface charge can often be measured, the surface potential is not easily accessible because part of the surface charge may be neutralised within the Stern layer. The electrokinetic potential (zeta potential or ζ-potential) is good as a first approximation for the potential at the Stern plane, but is probably no better than a first approximation.

(4) The simple model wih the deep primary minimum would make coagulation quite irreversible and would not allow repeptisation. However, repeptisation is the rule rather than the exception, and irreversibility is found only after the particles have been coagulated for some time.

(5) Time effects due to various relaxation processes in the double layer have not been incorporated into the theory. These effects are important, since the time of an individual collision, and even the characteristic coagulation time, may be shorter than the relaxation time for charge adjustment at the surface.

Some of the weaknesses of the theory of steric stabilisation are as follows:

(1) In the present state of the theory, quantitative applicability is limited.

(2) Adsorption of the stabiliser is obviously a key factor in the protection mechanism, but adsorbability is hard to predict.

3.5. Other methods of stabilising lyophobic colloids. In addition to the above mechanisms, "structural forces" due to modification of the water structure near interfaces may play a part in determining the stability of aqueous lyophobic colloids. It may be that these structural forces by themselves are not sufficiently strong, but they may supplement the other stabilising influences.

3.5.1. Hydration stabilisation or solvation stabilisation. Some studies of the stability of model colloid systems have shown marked deviations from the predictions of the DLVO theory. The presence of a hydration layer around the particles has been postulated as the cause of this deviation[119]. The hydration layer of the colloid particle is a layer of structured water molecules which are hydrogen-bonded to the ionic groups and dipoles of the adsorbed layer of stabiliser. There is evidence in the literature[120,121] to show the presence of a hydration layer near the solid surfaces. The extent of hydration is unknown. However, it is believed generally that the structuring of the water molecules near a surface is of short range.

There are four possible effects that the hydration layer might have upon the stability of a lyophobic colloid.

(a) The hydration layer may decrease the Hamaker constant, and hence the van der Waals attraction potential energy between the particles.

(b) The hydration from the interaction zone before destabilisation will result in an increase of free energy, and hence will bring into existence a repulsive force between the particles.

(c) Because of the volume restriction effect, the hydration layer will act as a mechanical barrier to prevent the particles from approaching one another closely.

(d) The interfacial free energy between the outer surface of the solvated particle and the dispersion medium is virtually zero.

All these effects promote stabilisation.

3.5.2. Depletion stabilisation. An additional mechanism has recently been proposed by Feigin and Napper[122]. These workers claim that colloid stability can be imparted by the presence of free polymer in solution in the dispersion medium. This type of stabilisation has been described as "depletion stabilisation" because it arises from the depletion of the concentration of segments of free polymer near to and between the surfaces of colloid particles.

When two spherical particles approach one another very closely, there will be almost complete exclusion of polymer molecules from between the surfaces. Thus, there is almost pure solvent in the interparticle space rather than polymer solution. The exclusion of polymer molecules from between two colloid particles is accompanied by an increase of free energy (mainly because the entropy is reduced), and this is the origin of the stability.

Depletion stabilisation differs from steric stabilisation in two important respects.

(a) The polymer that confers stability is free to move in solution instead of being attached or adsorbed onto the particle surfaces as is the case in steric stabilisation.

(b) Stabilisation imparted by free polymers appears to be of a kinetic kind, whereas that imparted by attached polymer may represent genuine thermodynamic stability of the colloid state.

CHAPTER FOUR

REVIEW OF PREVIOUS WORK ON SUBSTANCES WHICH FUNCTION AS BOTH INITIATORS AND STABILISERS FOR EMULSION POLYMERISATION REACTIONS

Recently several publications have appeared in which different workers claim to have synthesised substances which function as both initiators and stabilisers for emulsion polymerisation reactions. These authors apply the term "emulsifiers" to the substances synthesised; however, inasmuch as there is no evidence that all of the substances are emulsifiers, and since the substances prepared during the present project are apparently not emulsifiers, the term "stabilisers" will be used here to refer to such compounds.

Galibei et al[123] have initiated emulsion polymerisation using the water-soluble diacyl peroxide I,

$$RC(O)OOC(O)CH_2CH_2CO(OCH_2CH_2)_nO_2CCH_2CH_2C(O)OOC(O)R \quad (I)$$

where R is C_6H_{13} or C_7H_{15} and n has the values 1, 2 or 9. All these compounds are said to be water-soluble with surfactant properties. They have been used as effective catalysts for the emulsion polymerisation of styrene in the presence of the surfactant Tween 20. The results of Galibei et al show that the polymerisation rate depends upon the size of the hydrophilic and hydrophobic groups in I, being highest for R = C_7H_{15} and n = 9. Furthermore, the polymerisation rate was observed to increase to a certain level with increasing diacyl peroxide concentration. Above this concentration of initiator, the polymerisation rate decreased. The abstract of this paper offers no explanation for this observation. In a second paper[124], these workers studied the efficiency of the peroxide initiators given below in the bulk and emulsion polymerisation of styrene,

$$[RO_2C(CH_2)_nC(O)O]_2 \quad (II)$$

where R is Me or Et and n is 2 or 3, and I, where R is C_7H_{15} and n is 1, 9 or 13. They claim that in structure I the ester groups exert a stabilising influence on the peroxide group. Increasing the distance between the

peroxide and ester groups led to an increase in the thermal decomposition rate constant k_d. The decomposition of I is said to be faster than that of the monoperoxide since the peroxide groups of the former are chemically stabilised from only one side by an ester group. Increasing the number of oxyethylene groups in the central portion of I did not influence the initiating activity during bulk polymerisation but led to a rate increase during emulsion polymerisation.

Hydroperoxy derivatives of oxyethylated compounds have been synthesised by Ivanchev et al[125,126]. Thus a solution of 30 g of the monoester of

$$C_{18}H_{37}(OCH_2CH_2)_{20}OH \qquad (III)$$

with 4-methyl-4-cyclohexene-1,2-dicarboxylic acid in 200 ml of ethanol was ozonised at 0^o to give a hydroperoxide, a 0.01% aqueous solution of which had a surface tension of 44 dyne/cm. Stirring 100 ml of a 2% solution of this hydroperoxide (neutralised to pH 7) with 45 g of styrene for two hours at 60^o gave a polystyrene latex whose particle size was 0.07 μ. The molecular weight of the polymer contained in the latex is said to have been 1,230,000.

In addition, the compound

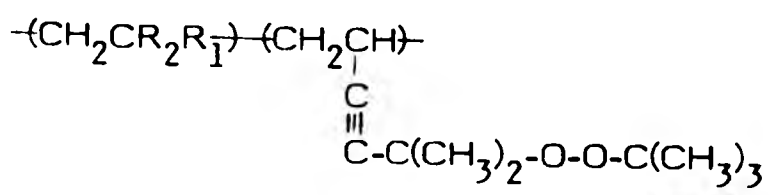
$$C_{18}H_{37}O(CH_2CH_2O)_{20}COCH(CH_2Ac)CH(CO_2H)CH_2CH(OEt)OOH \qquad (IV)$$

was used in the emulsion polymerisation of styrene. A solution of 0.01 g of IV in 100 ml of water had a surface tension of 44 dyne/cm. The critical micelle concentration of IV in water was found to be 0.0060 g/l. The polystyrene latices obtained using IV are said to have excellent resistance to electrolytes and to mechanical degradation[126].

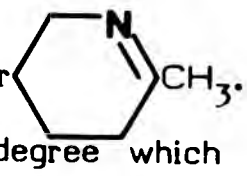
Ivanchev et al[127] claim that initiation in the emulsion polymerisation of styrene was localised in the growing polymer particles by using surface-active initiators and by bonding initiators to particle surfaces in seed polymerisation. Polymerisation in such systems was marked by low initiation efficiency, increased reaction order with respect to initiator,

little or no dependence of polymerisation rate on emulsifier concentration, high polymer molecular weight and narrow particle-size distribution of the latex. These pecularities are explained by Ivanchev et al as a consequence of the decreased rate of initiation and an anomalously low chain termination constant.

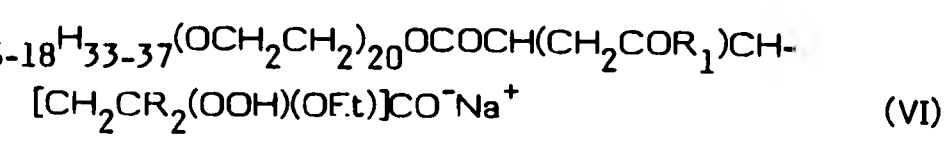
Voronov et al[128] have synthesised polymer surfactants containing peroxy groups which are said to be water-soluble. These surfactants were produced using unsaturated polymerisable peroxides and functional monomers. Their general formula is



(V)

where R_1 is CH_3 or H and R_2 is COOH or  These compounds are said to be surface-active to a degree which depends upon the composition and intrinsic viscosity of the peroxy oligomer. Aqueous solutions of these surfactants are said to be capable of initiating radical reactions in aqueous solutions.

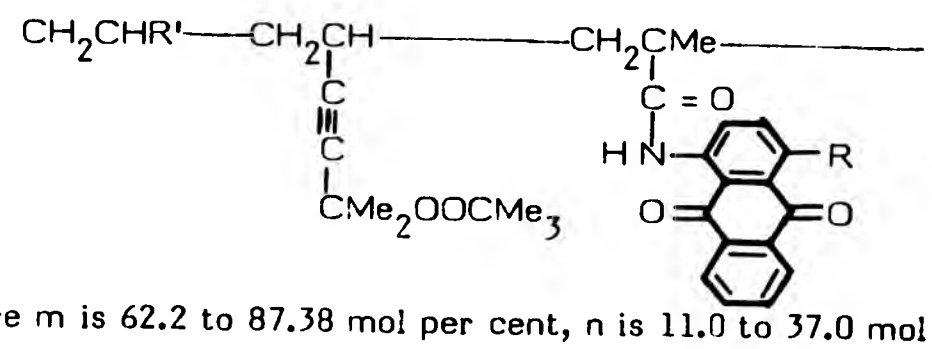
Polystyrene latices having a narrow particle-size distribution and containing a polymer of high molecular weight were obtained by Pavlyuchenko et al[129] using surface-active hydroperoxidic initiators such as



(VI)

where R_1 and R_2 are H or Me and R_1 is different from R_2.

Coloured latices have been obtained by Voronov et al[130] by polymerising vinyl monomers by heating in the presence of VII:



(VII)

where m is 62.2 to 87.38 mol per cent, n is 11.0 to 37.0 mol per cent, k is 0.2 to 2.3 mol per cent, R is CO_2H or 2-methylpyridin-4(or 5)-yl and R' is PhMe. Compounds of this type functioned simultaneously as stabilisers, initiators and anthraquinone dyes. There is no indication in the abstract of this paper that conventional surfactants were simultaneously used.

Polymeric stabilisers and initiators have been synthesised by Ershov et al[131]. A polymeric initiator-stabiliser with the structure

$$[CH_2CR(CO_2M)]_m[CH_2CR(CN)]_n[CH_2CH(C{\equiv}CCMe_2OOCMe_3]_p \qquad \text{(VIII)}$$

where R is H or Me, M is K, Na or NH_4, m is 50.7 to 80 mol per cent, n is 0 to 43.5 mol per cent and p is 2 to 20 mol per cent, was prepared by copolymerisation of (meth)acrylic acid, or its mixture with (meth)acrylonitrile, with $H_2C{=}CHC{=}CCMe_2\text{-}O\text{-}O\text{-}CMe_3$ in an aqueous medium in the presence of a radical-type initiator and a molecular-weight regulator. The abstract does not give any indication of how these compounds performed.

Heitz et al[132] have synthesised polymers containing azo groups as polymerisation stabilisers and initiators. Polymers containing blocks of ethylenically-unsaturated monomers and blocks of structure

$$[\text{-}CMe_2CO_2ZO_2CCMe_2N{=}N\text{-}]_n \qquad \text{(IX)}$$

where Z is C_1 to C_{36} alkylene, cycloalkylene, or arylene, or polyether, and n ranges from 1 to 10^4, are useful as combined initiator-stabilisers for the polymerisation of ethylenically-unsaturated monomers. The blocks containing azo groups were prepared by treating azobisisobutyronitrile with diols. Thus, a typical initiator-stabiliser polymer was prepared by polymerising 5 g of polyinitiator with 30 g of acrylamide in tertiary-

butanol. The initiator-stabiliser had a viscosity-average molecular weight between 60,000 and 70,000. A mixture of two parts of the above initiator-stabiliser, ten parts of vinyl acetate and 100 ml of water was polymerised for four hours at 70^{o} and then for one hour at 90^{o}, giving an emulsion which showed no settling after multiple freeze-thaw cycles.

Tsitrinbaum et al[133] have produced peroxidic polymeric initiator-stabilisers by the emulsion copolymerisation of vinylpyridines with dimethylvinylethylmethyl-t-butyl peroxide in an aqueous medium in the presence of initiators and stabilisers. According to the abstract of this paper, a variety of such initiator-stabilisers may be obtained by adding (meth)acrylic acid and different amounts of vinylpyridines to the reaction mixture at pH 0.2 to 6.0 and at a temperature of 20-40^{o}C in order to obtain a copolymer.

Voronov et al[134] claim to have synthesised linear random copolymers of quaternised 2-methyl-5-vinylpyridine and 2-(vinylethynyl)-2-propyl tert-butyl peroxide; these copolymers are reported to have crosslinking and initiating properties in acidic, neutral and alkaline aqueous media.

Voronov et al[135] have synthesised copolymers from acrylic acid (X) and tert-butyl dimethyl(vinylethynyl)methyl peroxide (XI) in methanol. In addition to being a comonomer, XI acted as a polymerisation initiator and chain-transfer agent. Neutralisation of the X-XI copolymer converted it into a water-soluble species if the concentration of carboxylate units in the copolymer was not less than 54.6 mol per cent. Water-soluble compounds of the copolymer were reported as having surfactant properties. The value of its critical micelle concentration depended upon its composition and molecular weight, though the abstract provides no typical values.

Further polymeric stabilisers containing peroxide groups have been synthesised by Voronov et al[136]. Water-soluble compounds containing peroxide side groups were prepared by radical cooligomerisation of dimethylvinylethynylmethyl tert-butyl peroxide with acrylic or methacrylic acids, or 2-methyl-5-vinylpyridine at 60-70^{o} in the presence of tert-dodecyl mercaptan as chain-transfer agent. It is stated that the

stabilisers produced exhibit solubilising properties and catalyse radical reactions in aqueous solutions.

Polymeric initiators have been obtained by Dicke and Heitz[137] by the acid-catalysed formation of azobisisobutyronitrile with tetraethylene glycol and 1,6-hexandiol. The kinetics of the decomposition of these polyazoesters were investigated by differential scanning calorimetry. An activation energy of E_a = 124.5 kJ/mol was reported. Polyazoesters can be obtained from azobisisobutyronitrile and diols. Polymers containing azo groups (prepolymers) are formed by partial decomposition of these polyinitiators in the presence of a monomer. The reaction of polyazoesters with hydrophilic monomers such as acrylamide and N-vinylpyrrolidone results in the formation of polymers which contain azo groups. These polymers are said to show surface-active properties. They can be used in emulsion polymerisation to form stable latices without the use of conventional surfactants and initiators.

Polyacrylamides which contain azo groups were used in the emulsion polymerisation of vinyl acetate as initiator-stabilisers. The rate/conversion curves for these reactions show the three reaction intervals typical of conventional emulsion polymerisations. A strong increase in the rate was observed up to about 15% conversion. This was followed by a constant rate up to about 65% conversion. Thereafter the reaction rate decreased. A plot of the log rate during Interval II versus the log of the concentration of prepolymer yielded a straight line of slope 1.02. The authors report that the rate of polymerisation is proportional to the concentration of the azo-group-containing polyacrylamide. The prepolymer combines the functions of initiator and stabiliser. The order of reaction found is, according to the authors, the "product" [sic; sc. 'sum'] of the orders expected for an initiator and a stabiliser independently.

Latices of polyvinyl acetate obtained using polyacrylamides which contain azo groups are said to be colloidally very stable. Polymers containing a high proportion of azo groups are, according to the authors, better suited to forming stable latices than, for example, peroxide initiators. These workers also found that feeding the monomer during the emulsion polymerisation reaction also increases the stability of the latices

obtained. Stable latices were also obtained by Dicke and Heitz[137] using monomers such as styrene, methyl methacrylate, acrylates and acrylonitrile.

Polymethacrylic acids which contained azo groups were obtained by partial decomposition of the initiator to 37% in the presence of methacrylic acid. The investigation of the surface tension of aqueous solutions of these prepolymers showed that azo-group-containing polymethacrylic acids have a surface activity comparable to that of other nonionic surfactants. The critical micelle concentration is reported as approximately 0.12 g/l. This methacrylic acid prepolymer can also be used as an initiator-stabiliser to form stable latices of polystyrene. In this case the latex particles are stabilised by a shell of solvated polymer and not by charge effects. Therefore it is not surprising that it is also possible to form stable latices of a polymer in an organic solvent using an azo-group-containing prepolymer which is soluble in that solvent.

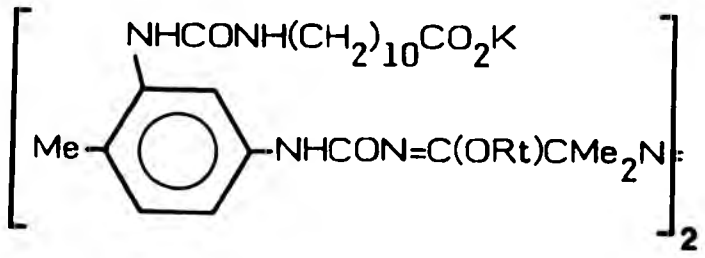
Schmidt and Roos[138,139] have obtained stable latices with low foaming tendencies and low electrolyte content by using stabilising azo initiators of the following general structures:

$$R'N{=}C(OR)CMe_2N{=}NCMe_2C(OR){=}NR' \qquad (XII)$$

$$R'NHC(=NR)CMe_2N{=}NCMe_2C(=NR)NHR' \qquad (XIII)$$

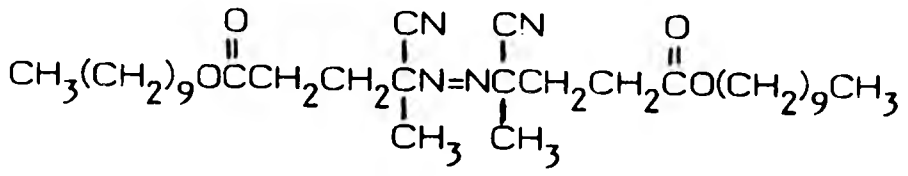
$$R'NHC(=NR')CMe_2N{=}NCMe_2C(=NR')NHR' \qquad (XIV)$$

In these structures, R is C_{1-4} alkyl, R' is CONHZNHCONHZ'COM or CONHZNHCONHZ'SO_3M, Z is a diisocyanate residue, Z' is phenylene or C_{5-12} alkylene, and M is Na, K or NH_4. In particular, these workers claim to have accomplished the copolymerisation of butylacrylate and styrene in water in the presence of 10% of the compound XV:



(XV)

The project described in this thesis had its origin in a research project carried out by the writer as part of the degree of M.Sc.[20]. It was surprisingly discovered that certain straight-chain esters of 4,4'-azobis-4-cyanopentanoic acid acted not only as initiators for conventional free-radical emulsion polymerisation reactions, but also as stabilisers for latices produced by the emulsion polymerisation of styrene in the absence of conventional surfactant. In other words, these azo compounds appeared to behave as stabilisers as well as as initiators. One such compound was the decyl ester of 4,4'-azobis-4-cyanopentanoic acid, XVI:



(XVI)

The behaviour of this compound was most unexpected, because the compound lacked an obvious hydrophilic component, which is normally considered to be essential, together with a hydrophobic component, for the stabilisation of latices and the support of emulsion polymerisation.

The effect of varying the alkyl group of the ester was investigated in the course of the M.Sc. project. The alkyl groups used were methyl, ethyl, n-hexyl, n-octyl, n-decyl, n-dodecyl, and n-tetradecyl. All the esters from octyl to tetradecyl were found to produce stable monodisperse polystyrene latices in the absence of added conventional surfactant. These latices contained polymers of various molecular weights. The molecular weights appeared to pass through a maximum with the decyl ester, after which the molecular weight decreased with increasing size of the alkyl group in the initiator. The molecular weights of the polystyrenes produced ranged from 10,000 for the methyl ester to 200,000 for the decyl ester. These emulsion polymerisation reactions were carried out at 70^{o} for two hours. The formulation used was 80 ml of water, 50 ml of styrene and 1.10×10^{-2} mol of the appropriate ester. The numbers of particles per unit volume were also found to be within the normal emulsion-polymerisation range, except perhaps in the case of the reaction initiated by the methyl ester. The values found ranged from 1.5×10^{13} cm^{-3} for the methyl ester to 1.5×10^{17} cm^{-3} for the dodecyl ester. These results showed a general increase in the number of particles per

unit volume as the chain length increased up to 10 to 12 carbon atoms, and then a decrease in the number of particles as the chain length of the ester increased further.

CHAPTER FIVE

PREPARATION OF DERIVATIVES OF 4,4'-AZOBIS-4-CYANOPENTANOIC ACID AND THEIR PRELIMINARY EVALUATION AS INITIATOR/STABILISERS

5.1. Introduction. This chapter includes the attempts made at preparing compounds that would act as initiator-stabilisers for the emulsion polymerisation of styrene. These compounds were all derivatives of 4,4'-azobis-4-cyanopentanoic acid and different hydroxy and amino compounds.

This chapter also includes the evaluation of the prepared compounds as initiators for the polymerisation of styrene in

(1) bulk polymerisation

(2) conventional emulsion polymerisation; i.e., when a surfactant is present

(3) emulsion polymerisation in the absence of conventional surfactant.

It is also necessary to note here a serious difficulty which was encountered at a later stage in the investigation. This occurred when the time came to choose suitable compounds for a detailed study of the properties of the more promising of these derivatives. It was then observed that esters prepared similarly to those which previously gave stable monodisperse latices in the absence of added conventional surfactant now failed to do so. The final part of this chapter describes investigations which were carried out in order to try to understand this phenomenon and to repeat the preparation of the original esters. The following abbreviations have been used throughout the text:

4,4'-AB-4-CPA = 4,4'-azobis-4-cyanopentanoic acid

4,4'-AB-4-CPC = 4,4'-azobis-4-cyanopentanoyl chloride

$FA(EO)_nH$ = fatty alcohol ethylene oxide condensate

$FA(EO)_nEs$ = ester of 4,4'-azobis-4-cyanopentanoic acid and $FA(EO)_n$

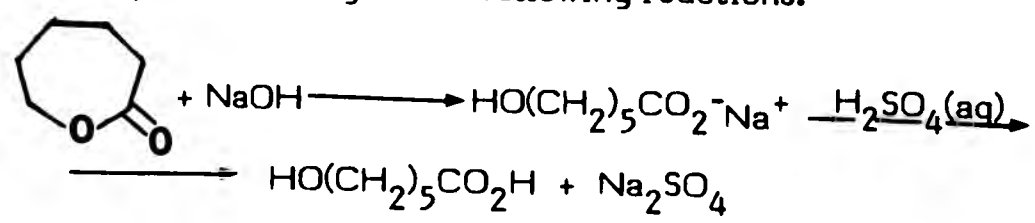
AZBN = azobisisobutyronitrile

5.2. Origin of chemicals.

CHEMICAL	ORIGIN	PURITY
4,4'-AB-4-CPA	Aldrich	97%
	Sigma	unspecified
phosphorus pentachloride	BDH	Analar
	Aldrich	technical
alcohols	Aldrich	97-99%
styrene	Aldrich	99%
nitrogen BOC white spot grade	BOC	99%
toluene	BDH	technical
ethyl acetate	Fisons	99%
triethylamine	Fisons	98%
dimethyl formamide	Aldrich	99%
benzene	BDH	Analar
	Fisons	Analar
laevulinic acid	Aldrich	95%
11-bromoundecanoic acid	Aldrich	99%
aldehydes	Aldrich	99%
amines	Aldrich	99%
aromatic hydroxy acids	Aldrich	99%
fatty alcohol ethoxylates	ABM Chemicals	technical

5.3. Preparation of starting compounds required for the preparation of derivatives of 4,4'-azobis-4-cyanopentanoic acid: hydroxy acids.

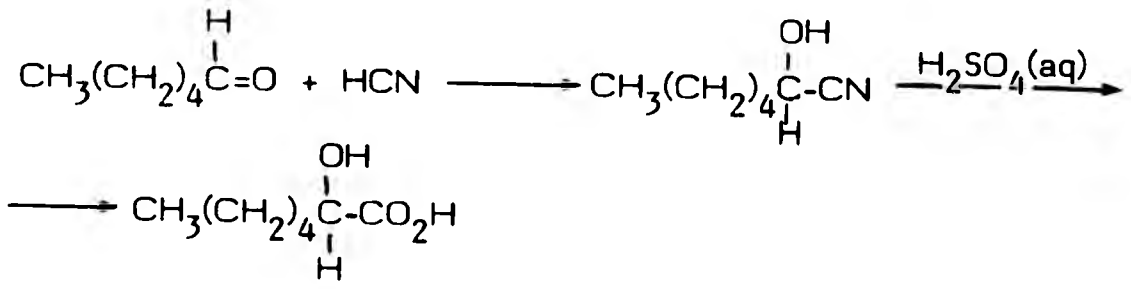
5.3.1. Preparation of 6-hydroxyhexanoic acid.[140-141] 6-hydroxy-hexanoic acid was prepared by opening of the ring of 6-hexanolactone by alkaline hydrolysis according to the following reactions:



The lactone (34 g/0.3 mol) was refluxed with sodium hydroxide (24 g/0.6 mol) in water for three hours. The water was evaporated off in order to establish whether any lactone remained. The residue contained no oil, and

since the lactone is an oily liquid, it was concluded that all the lactone had reacted. The sodium salt of 6-hydroxyhexanoic acid was obtained as a white solid. This solid was dissolved in water, and sulphuric acid added until the solution was acidic to litmus paper to form the corresponding hydroxy acid. The hydroxy acid was also a white solid; it was isolated by filtration. That 6-hydroxyhexanoic acid had been obtained was confirmed from its infrared spectrum. The acid was a waxy white substance.

5.3.2. Preparation of 2-hydroxyheptanoic acid.[142] An attempt was made to prepare 2-hydroxyheptanoic acid from hexanal by the following reactions:



Sodium cyanide was used as the source of hydrogen cyanide, the hydrogen cyanide being released by the addition of sodium metabisulphite.

Sodium metabisulphite (38 g/0.2 mol) was added at 30-40^{o}C over 15 minutes to a vigorously-stirred mixture of hexanal (30 g/0.3 mol), sodium cyanide (15 g/0.3 mol), ice (ca. 50 g) and distilled water (100 ml). After being stirred for a further 15 minutes, the mixture was cooled to 0^{o}C and the cyanohydrin produced was decanted off. Concentrated sulphuric acid was slowly added until the solution was acidic, in order to convert the cyanohydrin to the corresponding carboxylic acid. First a yellow oil and a water phase formed. The yellow oil turned brown overnight and then white crystals appeared. The crystals were filtered off; they were soluble in water but insoluble in dicholoromethane. The infrared spectrum of these white crystals revealed the presence of carbonyl and hydroxyl groups. This method gave a very poor yield.

5.3.3. Preparation of 2-hydroxyundecanoic acid.[143] An attempt was made to prepare 2-hydroxyundecanoic acid from decanal by reactions analagous to those used for the attempted preparation of

2-hydroxyheptanoic acid from hexanal. Decanal (40 g/0.3 mol) and sodium cyanide (15 g/0.3 mol) were stirred in water (5 ml) and ice (ca. 50 g). Sodium metabisulphite (38 g/0.2 mol) in water (50 ml) was added over a period of 20 minutes at room temperature. The reaction was allowed to proceed for two hours. The oil phase was decanted off and washed with diethyl ether. The diethyl ether was evaporated off, and concentrated hydrochloric acid added until the solution became acidic to litmus paper. White crystals of the cyanohydrin precipitated. These were filtered and washed with ether. The cyanohydrin was boiled in 20% alcoholic potassium hydroxide to convert it to the potassium salt of 2-hydroxyundecanoic acid, since Le Sueur[144] found that treating the cyanohydrin with hydrochloric acid did not convert it to the acid but to the amide instead. The solvent was evaporated off and a small amount of water was added. The potassium salt was converted to the acid by adding dilute sulphuric acid, until no more white solid precipitated. The yield was poor.

5.3.4. Preparation of 11-hydroxyundecanoic acid.[145] 11-hydroxyundecanoic acid was prepared from 11-bromoundecanoic acid by the following reactions:

$$Br(CH_2)_{10}CO_2H + 2\,KOH \longrightarrow HO(CH_2)_{10}CO_2^-K^+ + KBr$$
$$HO(CH_2)_{10}CO_2^-K^+ + HCl \longrightarrow HO(CH_2)_{10}CO_2H + KCl$$

11-bromoundecanoic acid (133 g/0.5 mol) was placed in a round-bottomed flask and 60 g/0.7 mol of potassium hydroxide dissolved in 500 ml of water was added. The mixture was refluxed for six hours. On cooling, a precipitate formed. The potassium salt of the 11-hydroxyundecanoic acid is only slightly soluble in cold water. The solid was filtered, and aqueous hydrochloric acid was added to the solution. The 11-hydroxyundecanoic acid precipitated. The structure of the product was confirmed by its infrared spectrum. Aqueous hydrochloric acid was also added to the first precipitate, in order to convert it to the acid, which was then recrystallised from hot water.

5.4. Instruments used in analysis. The following instruments were used to characterise the compounds prepared and latices obtained from them:

infrared spectrometer: Pye Unicam SP2000

NMR spectrometer: Burker WP 80 Multinuclear Pulse Transfer operated by John Crowder

elemental analysis: Perkin Elmer 240 Elemental Analyser operated by A. Rampersad

mass spectrometer: AEIMS9 Double-Focusing Model 502, operated by David Diggins

electron microscope: RCA type EMU 36, operated by J. S. Kotiyan

Coulter Nanosizer

gel permeation chromatograph and low-angle laser light scattering directed by Dr. S. Holding of RAPRA

du Nouy tensiometer: Cambridge Instruments

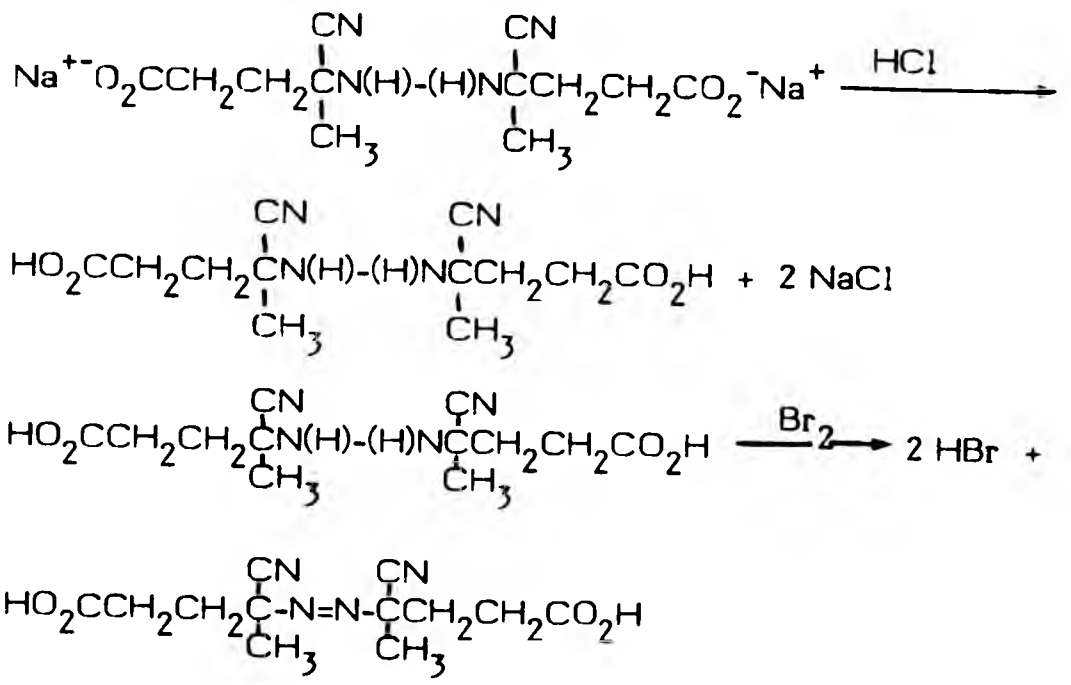
5.5. Preparation of 4,4'-azobis-4-cyanopentanoic acid and derivatives.

5.5.1. Preparation of 4,4'-azobis-4-cyanopentanoic acid. The procedure followed was that of Haynes and Waters[146]. To sodium cyanide (49 g /1 mol) and hydrazine sulphate (65 g/0.5 mol) in water (500 ml) at 50°C, laevulinic acid (116 g/1 mol) neutralised with sodium hydroxide (40 g /1 mol) in 200 ml of water was added over a period of 30 minutes. The solution was stirred vigorously. Bromine was added dropwise until the solution was deep yellow. The excess bromine was destroyed by adding sodium hydrogen sulphite. The colour returned to white/pale yellow. The white solid which had precipitated (108 g) was collected and washed once in ice water. The yield of 4,4'-AB-4-CPA obtained was 42%. The melting point range was 118-128 °C. The literature range is 115-127 °C[147].

The reactions which occurred during the preparation of 4,4'-AB-4-CPA are as follows:

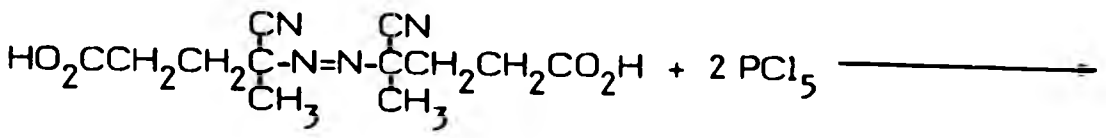
$$2\ Na^{+}\ ^{-}O_2CCH_2CH_2COCH_3 + NH_2NH_2H_2SO_4 + 2\ NaCN \longrightarrow$$

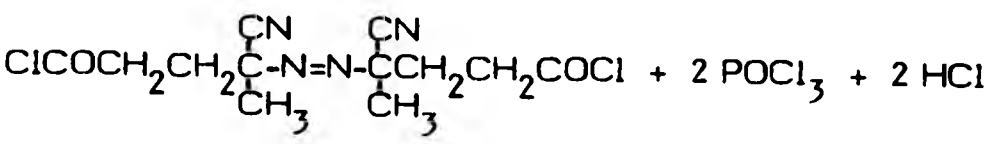
$$Na^{+}\ ^{-}O_2CCH_2CH_2\underset{\displaystyle CH_3}{\overset{\displaystyle CN}{\overset{|}{\underset{|}{C}}}}N(H)\text{-}(H)N\underset{\displaystyle CH_3}{\overset{\displaystyle CN}{\overset{|}{\underset{|}{C}}}}CH_2CH_2CO_2^{-}\ Na^{+} + Na_2SO_4 + 2\ H_2O$$



5.5.2. Preparation and characterisation of 4,4'-azobis-4-cyanopentanoyl chloride.

5.5.2.1. Preparation. 4,4'-AB-4-CPC was prepared by reacting 4,4'-AB-4-CPA (30 g/0.1 mol) with phosphorus pentachloride (60 g/0.3 mol) in benzene (300 ml) following the procedure of Smith[148]. The same procedure was used for the preparation of the 4,4'-AB-4-CPC which was used during the earlier MSc research project[20], to which reference has been made previously in this thesis.





The mixture was kept in an ice bath for 30 minutes, followed by two hours at room temperature. The solution was filtered and dried using a rotary evaporator at room temperature. The product was a pale yellow solid. This solid was washed twice with a mixture of diethyl ether and hexane (1:3). The solid was dissolved in a minimal volume of dichloromethane and the acid chloride was precipitated by adding hexane. A white substance

(22.15 g) of pungent odour was obtained. The yield of 4,4'-AB-4-CPC was 65%. The acid chloride thus prepared was used in the preparation of various derivatives of 4,4'-AB-4-CPC, such as esters and amides.

5.5.2.2. Characterisation. Some characterisation of 4,4'-AB-4-CPC prepared in this way was carried out during the earlier MSc research project[20]. The following techniques were used:

(1) elemental analysis

(2) infrared spectroscopy

(3) ^{13}C NMR spectroscopy

(4) mass spectrometry.

The following results were obtained:

Elemental analysis

	theoretical %	found %
C	45.42	45.58
H	4.42	4.78
N	17.66	17.78

Infrared analysis

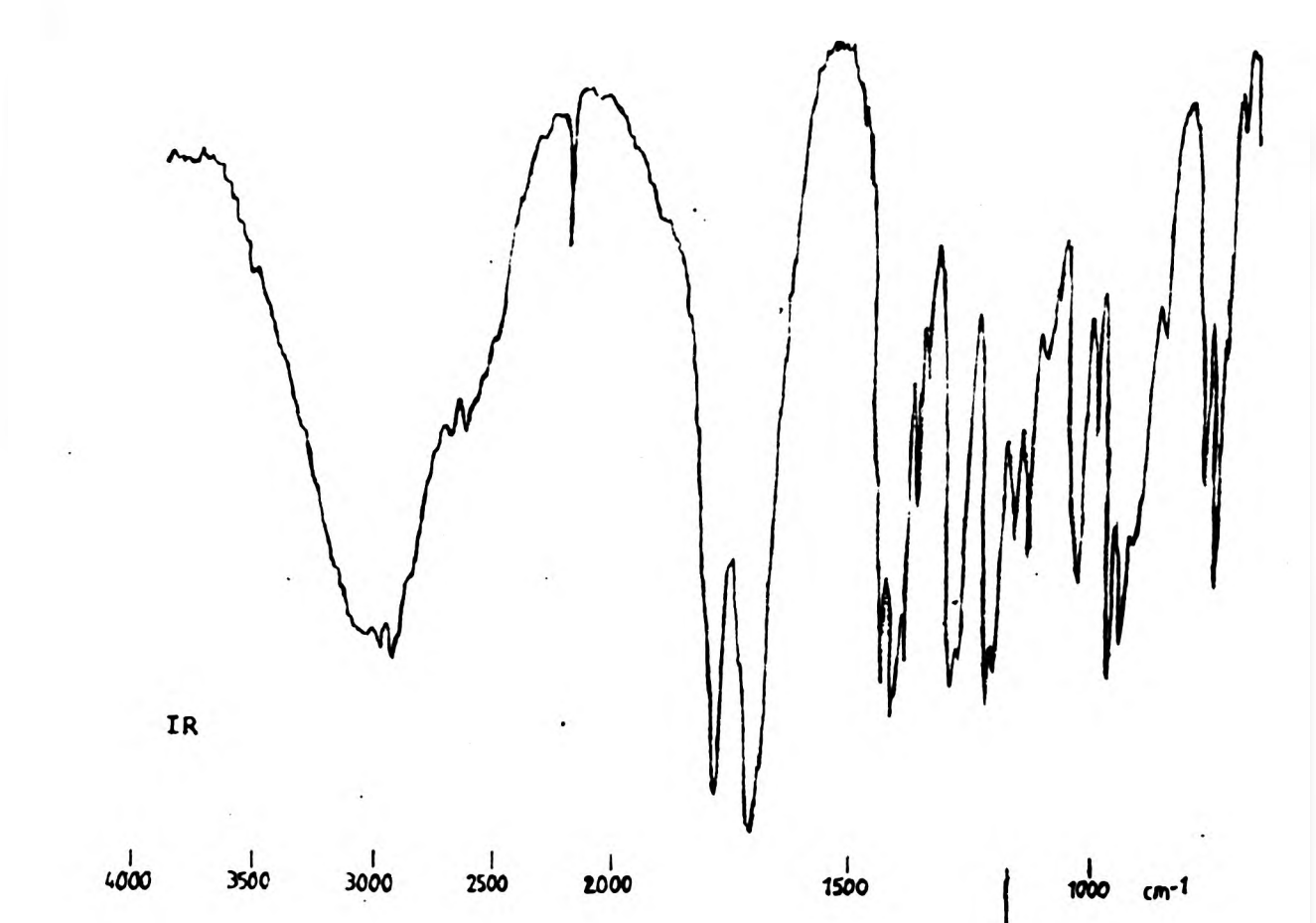
peaks (cm^{-1})	assignments
1730 } 1850 }	--COCl
2260	--CN
2940-3020	--CH

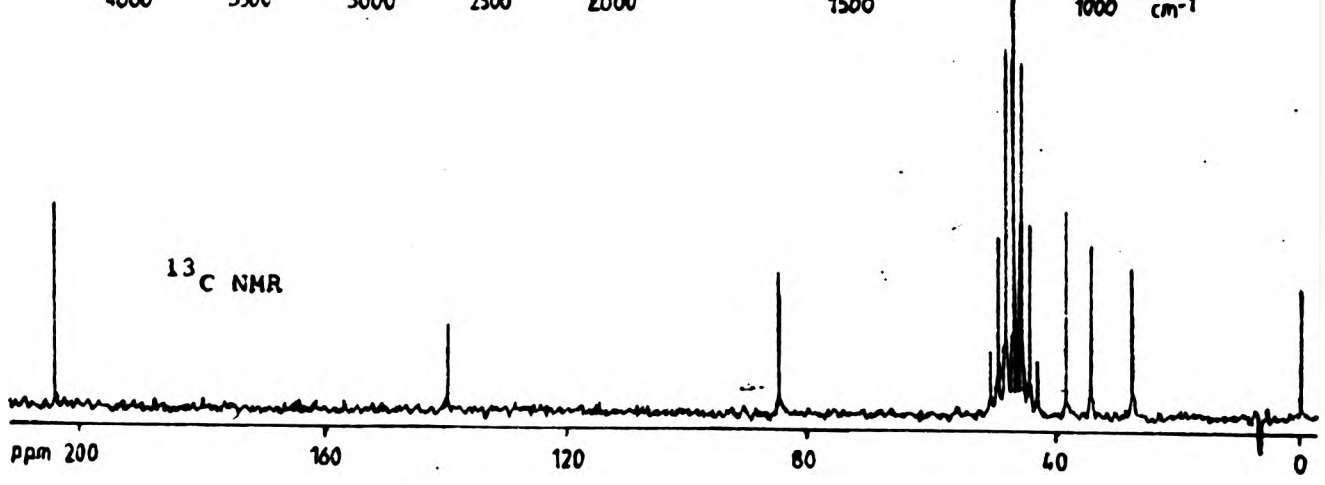
Figure 5.1(a) gives the spectrum obtained.

^{13}C NMR spectroscopy

peaks (ppm)	assignments
172	--COCl
118 doublet	--C≡N
71 doublet	C*
42-36	$--CH_3$
23-22	$--CH_2$

Figure 5.1(b) gives the spectrum obtained.





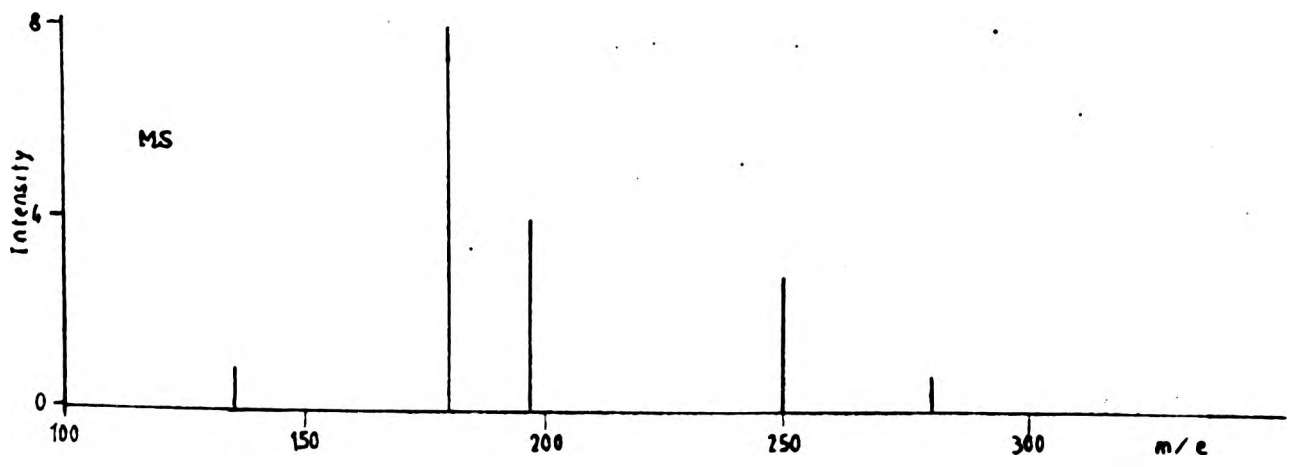


Fig. 5.1: Characterisation of 4,4'-azobis-4-cyanopentanoyl chloride by infrared, ^{13}NMR and mass spectroscopy.

Mass spectral analysis

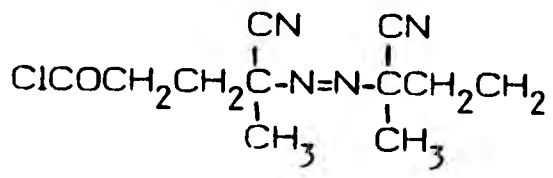
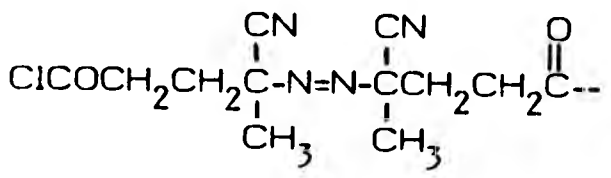
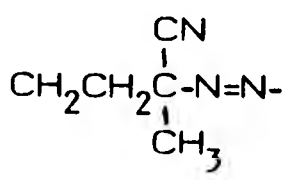
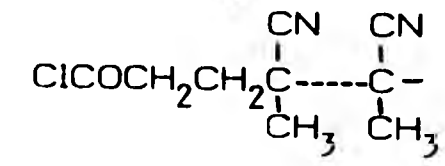
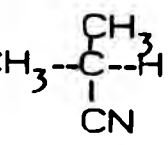
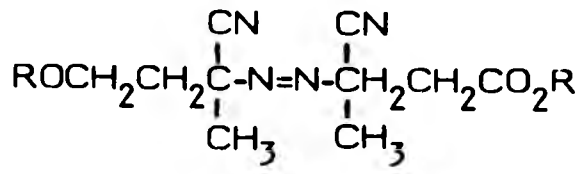
peaks (m/e)	fragments assigned
249 (s)	
280 (s)	
108 (s)	
197 (s)	

Figure 5.1(c) gives the spectrum obtained.

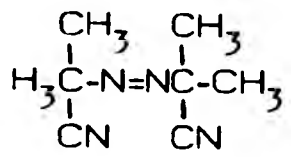
At the time of the MSc project, there was no indication that the substance prepared was anything but 4,4'-AB-4-CPC, and thus chlorine analysis was not carried out.

5.5.3. Synthesis of alkyl esters of 4,4'-azobis-4-cyanopentanoic acid by reaction of the acid chloride with various straight-chain alcohols.

5.5.3.1. Introduction. The compound  is slightly water-soluble[149], since the nitrile has some hydrophilic properties. Such a group close to an ester linkage might be expected to exhibit somewhat greater hydrophilic character than otherwise, as in, for example, the following compound:

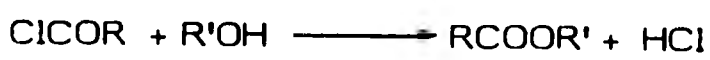


The esters might be expected to be slightly water-soluble and therefore to initiate emulsion polymerisation in the absence of conventional surfactant. However, the expected water-solubility is very low, especially for the higher esters. It should be noted, however, that although the compound $(CH_3)_2CHCN$ is slightly water-soluble, the solubility in water of the corresponding diazo compound

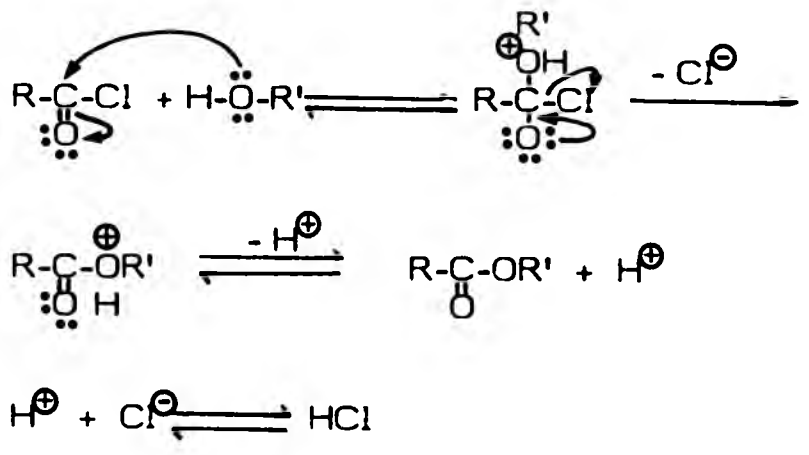


is said to be practically nil.

5.5.3.2 Mechanism of ester formation. The reaction between acid halides and alcohols is the best general method for the preparation of esters:



The reaction is of wide scope, and many functional groups do not interfere. The reaction mechanism is presumably nucleophilic substitution[151]:



5.5.3.3. Procedure. One mol of 4,4'-AB-4-CPC was reacted with 2 mol of alcohol. Triethylamine (2 mol) was used to remove the hydrogen chloride which forms in the reaction. The hydrogen chloride reacts with the triethylamine to form triethylammonium chloride, which is insoluble in the reaction medium. However, it was observed that a precipitate was also formed even if no alcohol was added to the acid chloride. It seems

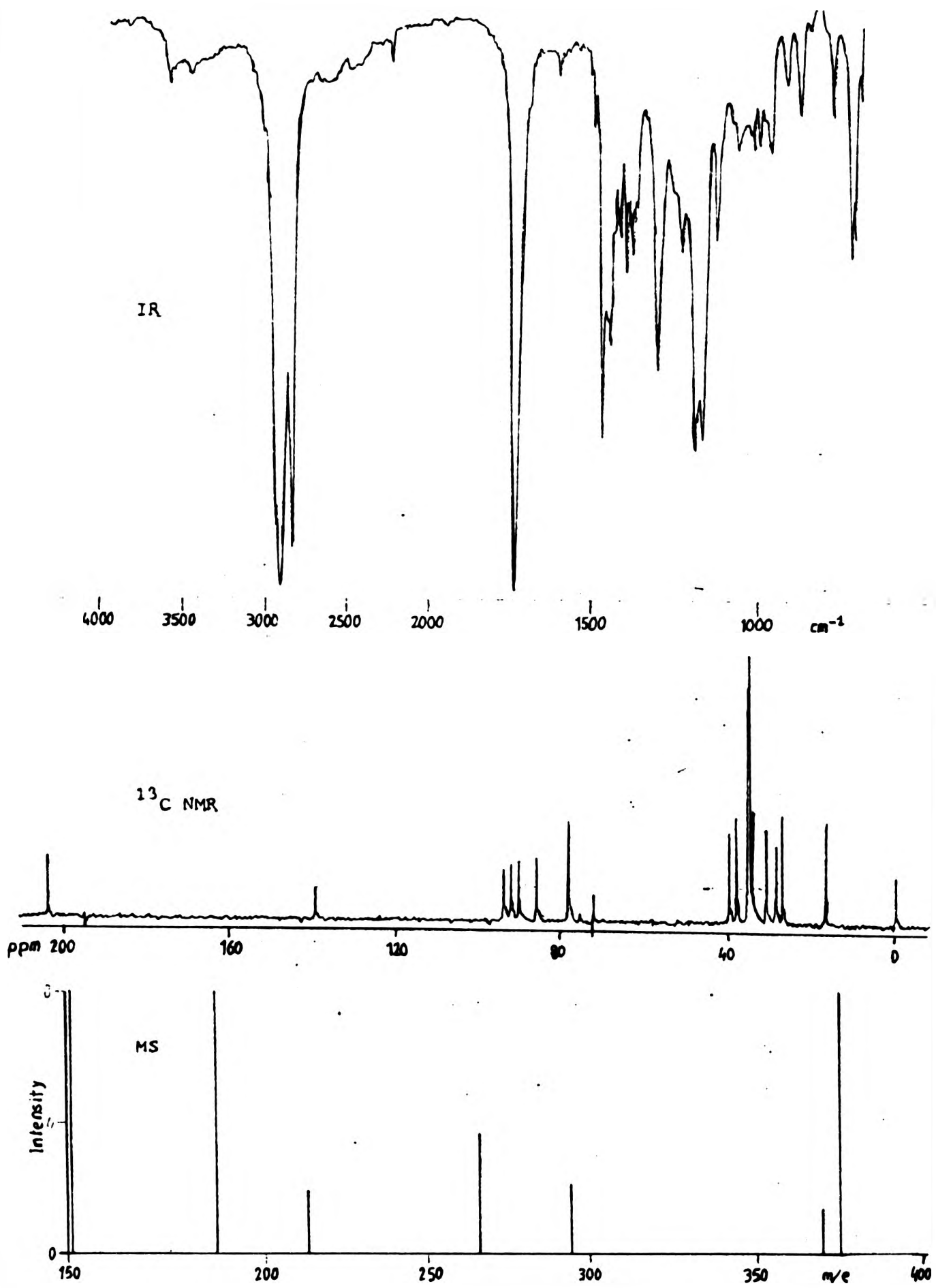


Fig. 5.2: Characterisation of the decyl ester derived from 4,4'-azobis-4-cyanopentanoic acid by infrared, ^{13}NMR and mass spectroscopy.

that tertiary amines can themselves react with acyl halides, the elements of hydrogen halide being lost with the formation of a ketene[152]:

$$RR'CH{\cdot}COX + R''_3N \longrightarrow RR'C{=}C{=}O + R''_3N{\cdot}HX$$

In order to avoid this reaction, the triethylamine was mixed with the alcohol and added dropwise to the well-stirred solution of acid chloride.

The esters were prepared by reaction in toluene (ca. 300 ml) at room temperature for one hour, although the precipitation of triethylammonium chloride was instantaneous. The triethylammonium chloride was removed by filtration. The esters were isolated by evaporating the solvent using a rotary evaporator at approximately 35°C. The esters were pale yellow waxes which had a typical ester-like odour. The yields of the esters obtained were approximately 90% of theoretical. Further purification of the esters was not attempted because they appeared to be thermally unstable.

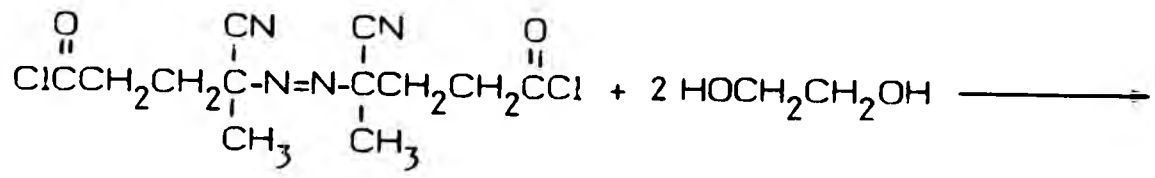
5.5.3.4. Characterisation. The results of attempts at spectral characterisation of the decyl ester carried out during the MSc research project[20] are given in Figure 5.2. All the evidence suggested that the preparation of the decyl ester of 4,4'-AB-4-CPA had been successful.

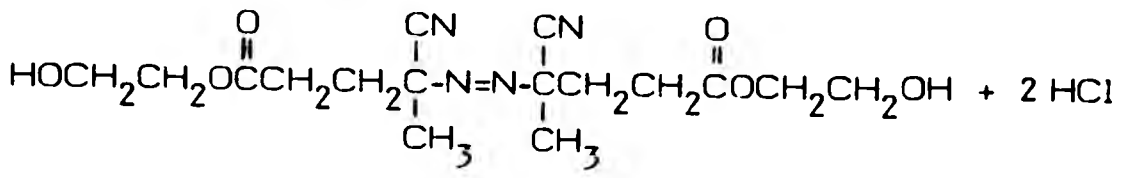
During the present project all the compounds prepared were subjected to infrared analysis to confirm their structures as far as possible. Further characterisation was left for a later stage, when the most promising compounds were to be studied in depth.

5.5.4. Preparation of esters of 4,4'-azobis-4-cyanopentanoic acid by reaction of the acid chloride with various other aliphatic hydroxy compounds.

5.5.4.1. Ester of ethan-1,2-diol (ethylene glycol). The preparation of this ester was identical to the preparation of esters of straight-chain alcohols; i.e., one mol of the acid chloride was reacted with 2 mol of the diol. The product was a brown waxy substance which was only sparingly soluble in toluene. A possible result of the reaction between 4,4'-AB-4-CPC and

ethan-1,2-diol is as follows:





The brown product was dissolved in ethyl acetate. The triethylammonium chloride was filtered off and the remaining solution evaporated using a rotary evaporator at approximately 35°C. It is believed that the ester is a mixture of the monomer, the dimer and some oligomeric species, since the infrared spectrum shows the presence of a carbonyl peak, a very weak OH band and a very strong CH band.

5.5.4.2. Ester of 2-ethyl-2-hydroxymethylpropan-1,3-diol (trimethylol propane). The procedure followed was that used for the preparation of esters from straight-chain alcohols. One mol of acid chloride was reacted with 2 mol of trimethylol propane. The product was a pink oil that turned slightly brown on standing. The oil was soluble in hot water but insoluble to any appreciable extent in either cold or hot styrene. The product was probably a mixture of the monoester, the diester and other substances.

5.5.4.3. Ester of 2,2-bis(hydroxymethyl)propan-1,3-diol (pentaerythritol). An identical preparative procedure was used for the preparation of this ester, or mixture of esters, to that which has been described above; i.e., one mol of acid chloride was reacted with 2 mol of pentaerythritol.

5.5.4.4. Esters of (i) 11-hydroxyundecanoic acid, (ii) z-12-hydroxyoctadec-9-enoic acid (ricinoleic acid) and (iii) fatty-alcohol ethoxylates. All these compounds are monohydroxy compounds. Esters were prepared from them by the procedure used for the preparation of esters from straight-chain alcohols; i.e., one mol of the acid chloride in toluene was reacted with 2 mol of the monohydroxy compound in the presence of 2 mol of triethylamine to yield the corresponding ester. All the compounds are

white waxes.

5.5.5. Preparation of esters of 4,4'-azobis-4-cyanopentanoic acid by reaction of the acid chloride with various cyclic compounds. The preparations of all the esters included in this section were carried out following the procedure employed for the preparation of the esters of the azo acid and the straight-chain alcohols; i.e., one mol of the acid chloride was dissolved in toluene (ca. 300 ml), and a mixture of 2 mol of the cyclic hydroxy compound and 2 mol of triethylamine was added dropwise to the solution. The triethylammonium chloride was filtered off, and the solution evaporated to dryness to obtain the ester.

5.5.5.1. Esters of (i) cyclohexanol, (ii) phenol, (iii) o-hydroxybenzoic acid and (iv) p-hydroxybenzoic acid. The ester of cyclohexanol was a yellow liquid, soluble in styrene but insoluble in water. The ester of phenol was a pink wax, soluble in styrene as well as in hot water, but insoluble in cold water. The yield of phenol ester obtained was 51%. The ester of o-hydroxybenzoic acid was a greenish resin that turned hard on standing. Its solubility in water and in styrene, both hot and cold, is practically nil. The ester of p-benzoic acid was a white solid which was also insoluble in styrene and in water, hot or cold.

5.5.5.2. Esters of (i) 1,3-dihydroxybenzene (resorcinol) and (ii) 1,3,5-trihydroxybenzene (phloroglucinol). The ester of resorcinol was an orange resin, soluble in hot water and insoluble in either hot or cold styrene. The yield of resorcinol ester obtained was 59%. The ester of phloroglucinol is a brown waxy solid, soluble in hot water but insoluble in styrene. The yield of phloroglucinol ester obtained was 66%.

5.5.6. Preparation of the potassium salts of the esters of 4,4'-azobis-4-cyanopentanoic acid and various hydroxy acids. The preparation of the potassium salts of several hydroxy acids was attempted in situ in the aqueous phase for the attemped emulsion polymerisation of styrene; the hydroxy acids used were (i) ricinoleic acid, (ii) 11-hydroxyundecanoic acid, (iii) o-hydroxybenzoic acid and (iv) p-hydroxybenzoic acid. The azo acid (1.1×10^{-2} mol) and potassium hydroxide (2.2×10^{-2} mol plus 10% excess) were added to the well-stirred water at $70^{o}C$ and allowed to react for

approximately two minutes. After this time, the styrene was added to the mixture in order to investigate the emulsion polymerisation behaviour.

However, the potassium salts of the esters of o-hydroxybenzoic acid and p-hydroxybenzoic acid failed to yield a latex when used as described above and their preparation was attempted in IMS. One mol of the ester was dissolved in IMS and 2 mol of potassium hydroxide added, since it too is soluble in IMS. The reaction was allowed to proceed for two hours. Both salts were white solids, insoluble in either water or styrene.

5.5.7. Preparation of amides.

5.5.7.1. Preparation of the decyl, dodecyl and tetradecyl amides of 4,4'-azobis-4-cyanopentanoic acid. Because the early work indicated that the esters of straight-chain alcohols could function as initiator-stabilisers for the emulsion polymerisation of styrene in the absence of conventional surfactants, the preparation of a range of similar straight-chain amides was also attempted. Two mol of the acid chloride were dissolved in ethyl acetate (ca. 300 ml). The amine (4 mol) was added to this solution at room temperature and allowed to react for one hour. The excess amine (2 mol) was used to react with the hydrogen chloride evolved.

Some of the decylammonium chloride was observed to dissolve in the reaction medium. Most of the decylammonium chloride was separated by filtration. The filtrate was then dried down in a rotary evaporator. Hexane was added to remove any unreacted amine. The amide was then purified by the addition of water in order to extract the remaining decylammonium chloride.

The dodecyl amide is insoluble in methanol, whereas the dodecylammonium chloride is soluble. Methanol was therefore added to the white solid and the mixture filtered. This procedure was repeated twice. The resultant white solid was then washed with water until no more dodecylammonium chloride remained, as evidenced by the absence of any precipitate when silver nitrate solution was added to the wash water. The yield of amide obtained was 82%.

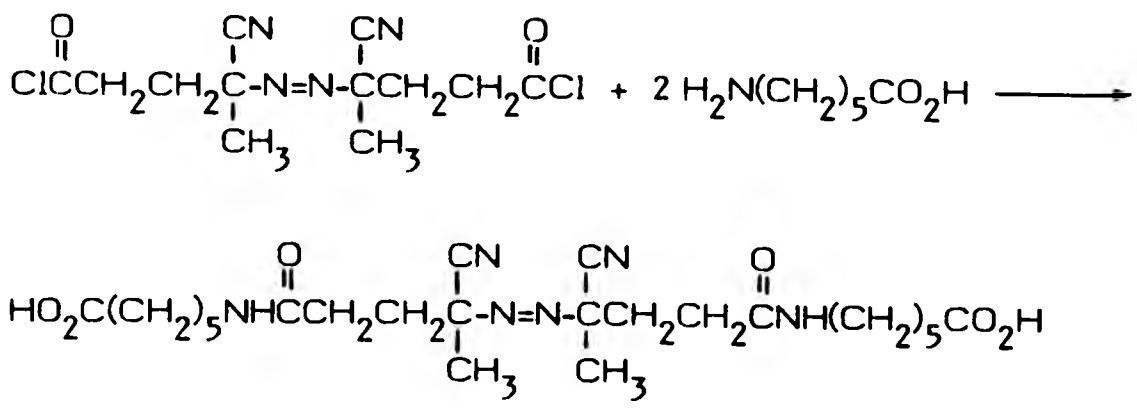
The same method was used for the preparation of the tetradecyl amide.

5.5.7.2. Attempted synthesis of the amide of 6-aminocaproic acid. The synthesis of amido acids is reported to have been accomplished by Stevens[153] using the reaction of a fatty-acid chloride with N-methylglycine in alkaline solution:

$$RCOCl + CH_3NHCH_2COONa + NaOH \longrightarrow RCON(CH_3)CH_2COONa + NaCl + H_2O$$

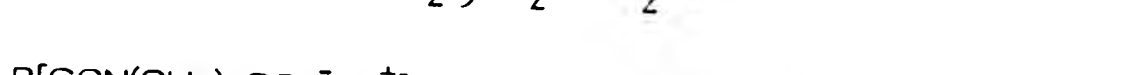
Also, derivatives of ϵ-aminocaproic acid were said to be synthesised by acylation of the amine function with the appropriate acid chloride, an example being 3,4,5-trimethoxybenzoyl chloride[154].

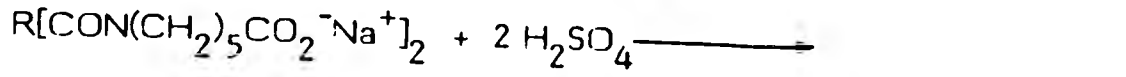
The synthesis of the amide of 4,4'-AB-4-CPA and 6-aminocaproic acid was also attempted. The first preparation involved the use of the azo acid chloride and the aminocaproic acid. 4,4'-AB-4-CPC (9.5 g/0.03 mol) was dissolved in ethyl acetate (ca. 300 ml). The amino acid (16 g/0.12 mol) was added in excess in order to remove the hydrogen chloride formed in the reaction.

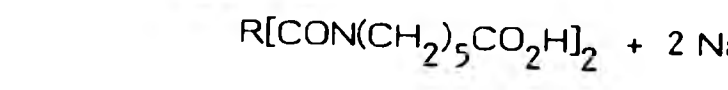


A white solid was obtained which dissolved in aqueous methanol. According to the infrared spectrum of the product, the desired compound had not been formed. The infrared spectrum was the exact replica of that of the 4,4'-AB-4-CPA.

The reaction was repeated in alkaline aqueous solution.

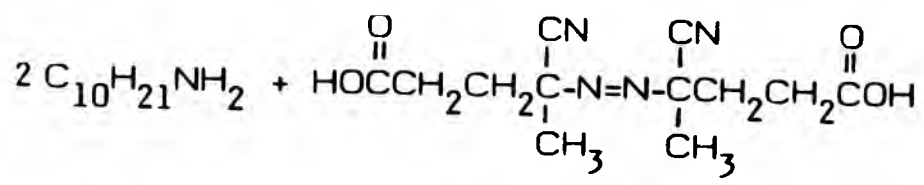


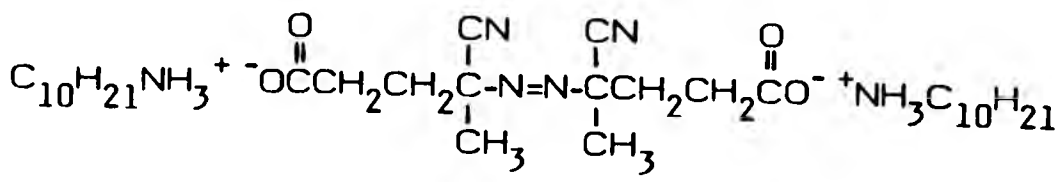


where R is 

However, no amide was obtained. The reaction was repeated again using glacial acetic acid as solvent, since the reaction was entirely soluble in it. But again the desired product was not obtained.

5.5.8. Synthesis of the decylammonium salt of 4,4'-azobis-4-cyanopentanoic acid. This salt was prepared by reacting 1-aminodecane with 4,4'-AB-4-CPA according to the following reactions:

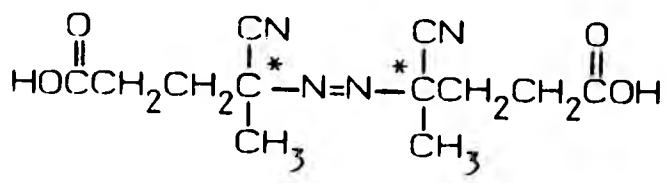




4,4'-AB-4-CPA (3 g/0.01 mol) was reacted with 1-aminodecane (3 g/0.02 mol). The reaction was carried out in acetone, in which both reactants are soluble. The solution turned brown. The solution was evaporated to dryness, and a brown-white solid remained. This solid was washed with ethyl acetate.

5.6. Separation of the meso and (±) isomers of 4,4'-azobis-4-cyanopentanoic acid.

5.6.1. Introduction. 4,4'-AB-4-CPA has two asymmetric carbon atoms in its structure:



Because of the symmetric nature of this molecule, individual molecules of the acid can exist in three stereoisomeric forms. These are as follows:

(i) The ++ form. This isomer rotates the plane of polarised light to the right.

(ii) The -- form. This isomer rotates the plane of polarised light to the left.

(iii) The meso form. In this form, one asymmetric carbon atom has the + conformation, and the other asymmetric carbon atom has the - conformation. Consequently, the molecule does not rotate the plane of polarised light.

Haines and Waters[146] found by titration analysis that the acid as normally prepared consists of 52% meso isomer and 48% racemic mixture of the ++ and -- forms; this racemic mixture is often referred to as the ( ) form. The acid as normally prepared is thus optically inactive.

The reason for wishing to separate the meso isomer from the racemic mixture was the failure of the amides to give a latex when used in the emulsion polymerisation of styrene. Since the amides were washed with water, there was a possibility of partial separation of the isomers from each other because of their different solubilities in water. Therefore separation of the meso form from the racemic mixture was attempted in order to examine their properties separately.

5.6.2. Procedure.[155] 4,4'-AB-4-CPA (30 g/0.1 mol) was stirred in 10% methanol in water (180 ml methanol, 1620 ml distilled water) for 24 hours. The mixture was filtered and the solid that remained was dried. The solid is, according to Haines and Waters[146], the meso isomer. This was

recrystallised by dissolving the solid in hot water (75-80^{o}C) and cooling the solution at room temperature. White crystals were obtained. The melting point was 132-133^{o}C. This compared favourably with the literature value of 134-135^{o}C[155] for the meso form. This substance was therefore identified as the meso form of the acid.

The filtrate was left for 24 hours at -3^{o}C. White crystals were obtained which were filtered and recrystallised from 334 ml of water at 60-65^{o}C and cooled at -3^{o}C. A white crystalline substance was obtained which melted over the range 117-118^{o}C. This compared favourably with the literature value of 118^{o}C[155] for the racemic mixture. This substance was therefore identified as the racemic mixture form of the acid.

The acid chloride and decyl ester of each isomer were prepared and investigated as initiator/stabilisers for the emulsion polymerisation of styrene in the absence of conventional surfactant. Both isomers gave very monodisperse latices. There were no detectable differences between the two decyl esters.

In view of the above result, it was concluded that it is unlikely that the removal of one isomer would make any significant difference to the abilities of the amides to function as initiator/stabilisers in emulsion polymerisation reactions in the absence of conventional surfactant.

5.7. Evaluation of derivatives of 4,4'-azobis-4-cyanopentanoic acid as initiators.

5.7.1. Introduction. As can be seen from the accompanying tables of results (Tables 5.1 to 5.14), of the various types of compounds prepared there were three which functioned effectively as initiator/stabilisers when used for the emulsion polymerisation of styrene in the absence of conventional surfactant, namely

(i) straight-chain esters of 4,4'-AB-4-CPA,

(ii) the fatty-alcohol ethoxylate esters, and

(iii) the salts of the esters of hydroxy acids.

Types (i) and (ii) are non-ionic, whilst type (iii) is ionic. Types (ii) and (iii), at least, contain a hydrophobic moiety in their molecule. It is not

surprising that the salts of the esters of long-chain hydroxy acids and the esters of the fatty-alcohol ethoxylates are able to function as stabilisers for polystyrene latices, since they contain a hydrophilic moiety, namely, the salt in the ionic compound and the long polyoxyethylene chain in the non-ionic fatty-alcohol ethoxylate esters. However, the esters of type (i) contain no such obvious hydrophilic moiety, and it is perhaps questionable whether they have a hydrophobic one. Nevertheless, it was observed that some straight-chain alkyl esters of 4,4'-AB-4-CPA appeared to be able to initiate the emulsion polymerisation of styrene and helped to stabilise a very monodisperse latex in the absence of conventional surfactant.

5.7.2. Purification of styrene for use as monomer in emulsion polymerisation experiments. The styrene as supplied by Aldrich Chemicals Ltd. was inhibited with 10-15 ppm p-tert-butylcatechol. In order to remove the inhibitor, the styrene was washed twice with 10% aqueous NaOH solution and then washed twice with doubly-distilled water. The first washing with NaOH gave a red colouration to the water phase, whilst the styrene phase turned yellow. Subsequent washings had no effect upon the colouration; the water layer remained colourless and the styrene yellow. The styrene was dried over calcium chloride for 24 hours, and then distilled under reduced pressure at approximately 60^{o}C. The colourless, distilled styrene was stored in a refrigerator at -20^{o}C.

5.7.3. Purification of distilled water for use in emulsion polymerisation experiments. Distilled water from the laboratory supply was used after it had been distilled once again. The doubly-distilled water was deaerated by bubbling nitrogen through it overnight, at the same time removing any carbon dioxide that might have been dissolved in the water.

5.7.4. Recipes used in the various types of polymerisation experiments. Kinetic studies.

(i) Bulk polymerisation experiments

The formulation employed for the bulk polymerisation of styrene when the esters derived from 4,4'-AB-4-CPA were used as initiators was as follows:

styrene	50 ml
ester	1.48 x 10^{-3} mol

The styrene and the ester were placed in a test tube which was then stoppered. The test tube was placed in a water bath at 70°C for a period of two hours. The polymer was precipitated by pouring the reaction solution into a large excess of methanol. The polymer was filtered, dried and weighed to estimate the yield.

The kinetics of bulk polymerisation of styrene were followed for two cases. In both cases, 1.1×10^{-2} mol of initiator was used. In the first case, the initiator used was AZBN, and in the second case, the initiator used was the decyl ester of 4,4'-AB-4-CPA. 50 ml of styrene and the corresponding amount of initiator were divided among ten test tubes, which were then stoppered and placed in a water bath at 52°C. At given intervals, the test tubes were emptied into 100 ml of methanol to which approximately five drops of tert-butylcatechol solution had been added. The polymer was filtered off, dried and weighed to estimate the yield. Fig. 5.3 gives the results obtained for conversion v. time for the two reactions.

(ii) Conventional emulsion polymerisation experiments, i.e., in the presence of a conventional surfactant.

The formulation used when an ester derived from 4,4'-AB-4-CPA was used as an initiator and sodium lauryl sulphate was used as a stabiliser was as follows:

styrene	50 ml
water	80 ml
ester	1.48×10^{-3} mol
sodium lauryl sulphate	1.10×10^{-2} mol

The sodium lauryl sulphate and the ester were dissolved in the water and then added to the reaction flask, which was fitted with a stirrer, a condensor and a nitrogen inlet. Finally the styrene was added. The reactions were carried out in a water bath at 70°C, under nitrogen, with constant stirring for a period of two hours. The polymers in the latex were precipitated by pouring a small volume of the latex (10 ml) into excess methanol (200 ml). The polymer was dried and weighed in order to estimate the yield. The pH of the latices obtained was neutral.

(iii) Emulsion polymerisation experiments using recipes which did not contain conventional surfactant.

When the emulsion polymerisation of styrene was carried out using the esters derived from 4,4'-AB-4-CPA as initiators as well as stabilisers, i.e., in the absence of added conventional surfactant, the formulation used was as follows:

styrene	50 ml
water	80 ml
ester	1.1×10^{-2} mol

The procedure was as described in (ii) above. The polymer could be obtained in the case of the latex produced by the esters of straight-chain alcohols and 4,4'-AB-4-CPA by destabilisation of the latex with methanol, acid, base or even sodium chloride solution. The pH of the latex produced was neutral.

The conversion-time curve for the emulsion polymerisation of styrene when using the decyl ester of 4,4'-AB-4-CPA as initiator/stabiliser in the absence of conventional surfactant is given in Fig. 5.4. Initially, it was intended to obtain conversion-time curves by withdrawing samples from the reaction flask in which the polymerisation was taking place, and evaporating the samples to dryness to obtain polymer yields. Such yields proved to be erratic, mainly because the system was not completely macroscopically homogeneous. Consequently, the procedure was modified to the following: The ester was dissolved in the water and the styrene was added to it. The mixture was divided among ten bottles and placed in a water bath at $52^{o}C$. The bottles were rotated end over end to ensure proper mixing. At given intervals, one bottle was taken out and the polymer was precipitated in methanol to which approximately five drops of p-tert-butylcatechol had been added. The polymer was filtered, washed with methanol, dried and weighed to estimate the yield.

When the fatty-alcohol ethoxylate esters were used as initiator/stabilisers in the absence of conventional surfactant, the precipitation of the polymer produced was achieved by addition of acidified methanol. Neutral methanol did not destabilise the latex. The pH of these latices was also neutral.

When the potassium salts of the esters of the hydroxy acids and 4,4'-AB-4-CPA were used as initiator/stabilisers, the pH of the resulting latex was approximately 8, since excess KOH was used. The destabilisation of the latex could be achieved by methanol, acid or base.

5.7.5. Properties of the latices formed using various azo initiator/stabilisers.

5.7.5.1. Introduction. The polymerisation of styrene was carried out in water in the presence of each of the azo compounds prepared as described in the preceding section, in order to ascertain whether or not they would act simultaneously as initiators and stabilisers. In some cases, the polymerisation was successful and the end product appeared to be a latex. When a latex was obtained, the following properties of the latex were determined:

(a) average particle size;
(b) particle-size distribution;
(c) number of particles per unit volume;
(d) surface tension (in some cases).

5.7.5.2. Determination of latex particle size. An indication of particle-size distribution for each latex was obtained as follows: An electron micrograph of each latex was taken using an electron microscope at knowun magnification. Each negative was then examined under a ten-power magnifying lens, and in each case the diameters of 75 arbitrarily-chosen particles were measured to the nearest millimeter and recorded as "millimeters read". For each photograph examined in this way,the volume-average particle diameter, d_v, was calculated as

$$d_v = \sqrt[3]{\frac{\Sigma n_i d_i^3}{\Sigma n_i}}$$

where n_i is the number of particles having diameters within a range whose central value is d_i. The value of d_v obtained was then converted into diameter in nanometers using the knowun magnification.

5.7.5.3 Determination of particle-size distribution. Histograms were constructed by plotting the frequency of appearance of each value of particle diameter d_i against the particle diameter value d_i. Figure 5.6 gives some of the histograms plotted.

5.7.5.4. Determination of number of particles per unit volume. The number of particles per unit volume, N, was calculated for each latex as follows[156]:

$$N = \frac{6w}{d_v^3 \pi \rho}$$

where is the density of polystyrene (1.05 g cm^{-3}[157]) and w is the mass of polymer per unit volume of latex.

5.7.5.5. Determination of surface tension. The surface tension of the air-water interface of some of the latices was measured using a du Nouy Tensiometer, applying the method specified in BS4561:1970. The temperature of the experiment was $25^{o}C \pm 1^{o}C$. Three determinations were made for each latex, and the average value was taken.

5.8. Discussion of preliminary results.

5.8.1. Introduction. The syntheses of 4,4'-AB-4-CPA and its acid chloride were successfully carried out, as indicated by infrared analysis and melting point for the acid and by infrared analysis for the acid chloride. The infrared spectrum and the melting point of the acid prepared were virtually identical to those of the acid purchased from commercial sources which was also used in these experiments. During the MSc project[20], the acid chloride was subjected to elemental analysis, and to characterisation by ^{13}C NMR and mass spectroscopic techniques. All the evidence confirmed the identity of the acid chloride. The same techniques were used for the analysis of the esters which were synthesised during the MSc project, and which were to be used in this project also, but only infrared analysis was carried out for every compound in this project, since at the time it was thought unnecessary to characterise every compound fully. Full characterisation was left for a later date when it

was intended to characterise extensively those compounds which were to be used in more detailed kinetic studies.

The nonyl, decyl, undecyl and hexadecyl esters behaved as stabilisers in the absence of conventional surfactant, giving very monodisperse and stable latices. It is interesting to note that, unexpectedly, all of them appeared to be at least partially soluble in warm water, whilst the esters of ethanol and octadecanol were not soluble in hot water to any appreciable extent, although they did melt. These latter compounds did not give a latex, but they did polymerise styrene in bulk. The presence of free hydroxyl groups in the azo ester, rather surprisingly, did not seem to enhance their water solubility, and esters containing acyclic, cyclic or aromatic hydroxyls did not give a latex. Even the potassium salts of esters of aromatic hydroxy acids were water-insoluble and did not yield a latex.

Although the decyl, dodecyl and hexadecyl esters did form latices, the decyl, dodecyl and tetradecyl amides were water-insoluble and did not form latices. The amides are able to effect polymerisation in bulk but not in surfactant-free emulsion polymerisation. One would expect the esters to behave very similarly to the amides and to be water-insoluble, but in fact the former appear to be partly water-soluble and to give latices when used as initiators in the polymerisation of styrene in the absence of conventional surfactant.

The potassium salts of long-chain aliphatic azo hydroxy acids are water-soluble and serve as initiator/stabilisers for the emulsion polymerisation of styrene.

It seems that solubility in water is an essential requirement if a compound is to function as an initiator/stabiliser in the emulsion polymerisation of styrene.

The decyl and hexadecyl esters produced stable latices with no coagulation. Although the nonyl and undecyl esters gave higher conversions, there was some considerable coagulation around the stirrer.

Of the esters prepared from the fatty-alcohol ethoxylates, those prepared from $FA(EO)_{24}H$ and $FA(EO)_{60}H$ gave the most promising latices under the conditions used. The other fatty-alcohol ethoxylate esters formed two layers of different proportions, depending on the fatty-alcohol ethoxylate used, when the stirring was stopped. Some of the $FA(EO)_{24}Es$ latex destabilised and formed a solid but the rest remained as a stable latex. $FA(EO)_{60}Es$ was observed to form a very foamy latex. $FA(EO)_{10}Es$, $FA(EO)_{14}Es$ and $FA(EO)_{24}Es$ showed inverse solubility; i.e., they were more soluble in water at room temperature than at the temperature of polymerisation.

A third group of successful initiator/stabilisers comprised the potassium salts of esters of ricinoleic acid and 11-hydroxyundecanoic acid and 4,4'-AB-4-CPA. Both ester salts gave very stable latices.

In the case of esters of straight-chain alcohols and 4,4'-AB-4-CPA, it is possible that stabilisation might be a consequence of the presence of carboxylated end-groups resulting from the hydrolysis of the esters. However, although the undecyl ester and potassium undecanoate ester form latices, the undecyl ester acid in the absence of emulsifier forms no latex. This last compound resembles the undecyl ester, except that it contains carboxylic acid groups.

5.8.2. Effect of azo compounds as initiators for the bulk polymerisation of styrene. Almost all of the azo compounds investigated are effective as initiators for the bulk polymerisation of styrene. The results obtained resemble those for the bulk polymerisation of styrene when AZBN is used as initiator under identical conditions. The behaviour of these azo derivatives as initiators for bulk polymerisation is generally as expected. When a constant weight of ester is used, as in the case of the fatty-alcohol ethoxylate esters, the yield decreases as the number of polyoxyethylene units increases. This is, of course, to be expected, since the molar concentration of initiator also decreases. However, there are a few compounds which are not very effective as initiators for bulk polymerisation. All the azo compounds that give poor yields when used as initiators for the bulk polymerisation of styrene are of low solubility in styrene. Hohenstein and Mark[158], drawing upon data published by other

workers, have made the reasonable suggestion that initiation will take place where the monomer and initiator can meet. Thus, it seems reasonable to conclude that it is not the effectiveness of radical generation that retards the polymerisation, but the ability of the radicals to reach the styrene molecules. Possibly these compounds, and certainly the others, generate radicals effectively.

5.8.3. Effect of azo compounds as initiators for conventional emulsion polymerisation of styrene. All the azo compounds prepared in this project act as effective initiators for the emulsion polymerisation of styrene when sodium lauryl sulphate is used as a colloid stabiliser. Also, the emulsion polymerisation of styrene occurred satisfactorily when AZBN was used as initiator and sodium lauryl sulphate as stabiliser. Furthermore, all the results, including that obtained when AZBN was the initiator, are remarkably similar. This confirms the statement made earlier that all the compounds generate radicals effectively.

Hohenstein and Mark[158] claim that, if the monomer is hydrophobic, such as styrene, and the initiator is oil-soluble, such as AZBN, the extreme case of suspension polymerisation occurs. The results obtained by Al-Shahib and Dunn[159], as well as those obtained during this project, show that even in such cases emulsion polymerisation can, and indeed does, occur.

Al-Shahib and Dunn[159] have shown that oil-soluble initiators in the presence of a conventional surfactant can produce rates of emulsion polymerisation similar to those obtained with water-soluble initiators. Although radicals are generated in pairs in the oil phase, these workers suggest that the escape of a radical to the aqueous phase leaves an isolated radical in the oil phase. The presence of a radical close by will result in bimolecular termination, giving polymers of low molecular weight. Dunn et al[160] have further suggested that transfer of a radical from an initiator to an emulsifier molecule which is subsequently desorbed into the aqueous phase could increase the escape efficiency, and thus increase the rate of initiation. In their view, the probability of an emulsifier radical being desorbed before undergoing further reaction may be the critical factor.

5.8.4. Effect of azo compounds as initiators for the emulsion polymerisation of styrene in the absence of conventional surfactant. All of the compounds prepared during this project behaved as effective initiators for the emulsion polymerisation of styrene in the presence of conventional surfactant, but a few of those compounds also behaved as effective colloidal stabilisers for the polystyrene produced from the reaction in the absence of conventional surfactant.

Of the esters prepared from the straight-chain alcohols and 4,4'-AB-4-CPA, the nonyl, decyl, undecyl and hexadecyl esters gave stable monodisperse polystyrene latices.

During the earlier MSc project[20], the methyl, ethyl, hexyl, octyl, decyl, dodecyl and tetradecyl esters of 4,4'-AB-4-CPA were prepared. The results showed that the octyl, decyl, dodecyl and tetradecyl esters gave stable, monodisperse polystyrene latices. When the alkyl chain length of the ester was below eight carbon atoms, the effectiveness of the ester as a colloid stabiliser was greatly reduced.

The yields, particle sizes and particle numbers for the successful latices obtained using the esters of straight-chain alcohols and 4,4'-AB-4-CPA in this project and those results obtained during the MSc research project are compared in Table 5.15.

	Present Project			MSc Project		
	Yield (%)	Part. Size (nm)	Particle Number (dm^{-3})	Yield (%)	Part. Size (nm)	Particle Number (dm^{-3})
octyl ester of 4,4'-AB-4-CPA	not prepared			48	140	4.61×10^{17}
nonyl ester of 4,4'-AB-4-CPA	48	127	1.95×10^{17}	not prepared		
decyl ester of 4,4'-AB-4-CPA	35	126	1.33×10^{17}	37	160	2.11×10^{17}
undecyl ester of 4,4'-AB-4-CPA	42	112	2.85×10^{17}	not prepared		
dodecyl ester of 4,4'-AB-4-CPA	not prepared			60	130	1.52×10^{17}
tetradecyl ester of 4,4'-AB-4-CPA	not prepared			64	180	1.51×10^{15}
hexadecyl ester of 4,4'-AB-4-CPA	15	126	5.09×10^{16}	not prepared		

Table 5.15: Comparison of results for polystyrene latices prepared during present project and MSc project using n-alkyl esters of 4,4'-AB-4-CPA as initiator/stabilisers

During the MSc project, it was also found that there was a trend in the molecular weights obtained. The highest molecular weight was observed to be that of the polystyrene obtained using the decyl ester as initiator/stabiliser (ca. 300 000 using membrane osmometry). The molecular weight of the polymer decreased as the chain length of the ester either increased or decreased from ten carbon atoms.

The molecular weights of the polymers prepared during the present project using the n-alkyl esters of 4,4'-AB-4-CPA as initiator/stabilisers have not been determined because of lack of time.

The results of both projects show that the octyl, nonyl, decyl, undecyl, dodecyl, tetradecyl and hexadecyl esters of 4,4'-AB-4-CPA can behave

not only as initiators but also as stabilisers for the emulsion polymerisation of styrene in the absence of conventional surfactant. The yields are comparable. The particle sizes are small, being well within the range of sizes which are typical of conventional emulsion polymerisation reactions, and the particle number is typical of that found in the product of conventional emulsion polymerisation reactions. Table 5.15 shows that the reproducibility of the results for the latex obtained with the decyl ester (the only ester used in both projects) is satisfactory.

Thus, it can be concluded that these initiator/stabilisers, in spite of being soluble in styrene and in spite of lacking an obvious hydrophilic moiety, do not initiate suspension polymerisation but rather true emulsion polymerisation.

How colloidal stability is conferred and how one radical leaves the polymerisation locus in order to avoid almost instantaneous termination, and thus presumably the formation of oligomers instead of polymers, is not clear at present.

The second group of successful initiator/stabilisers prepared during this project comprises the 4,4'-AB-4-CPA esters of the fatty-alcohol ethoxylates which are commercially available as the "Texofor A" series. To a greater or lesser extent, all the esters gave some polystyrene latex. The most successful initiator/stabilisers of this type for the emulsion polymerisation of styrene were $FA(EO)_{24}Es$ and $FA(EO)_{60}Es$. The temperature of the polymerisation was $70^{o}C$, as before. $FA(EO)_{2}Es$, $FA(EO)_{6}Es$ and $FA(EO)_{10}Es$ are insoluble in water at room temperature as well as at $70^{o}C$. $FA(EO)_{14}Es$, $FA(EO)_{24}Es$ and $FA(EO)_{30}Es$ show inverse solubility behaviour. $FA(EO)_{45}Es$ and $FA(EO)_{60}Es$ do not show inverse solubility behaviour over the temperature range studied. It is believed that some of the results obtained when these esters were used as initiator/stabilisers may have been the consequence of a mixture of emulsion, suspension and perhaps some bulk polymerisation; and because of the difficulties in separating them, the yields given in the results section are of the total polymer produced, irrespective of the polymerisation mechanism followed.

It is not surprising that some of these initiator/stabilisers help to stabilise the latex produced in the surfactant-free emulsion polymerisation of styrene, since they possess a strongly hydrophobic moiety and a hydrophilic moiety made up of oxyethylene units.

Finally, the last group of successful initiator/stabilisers prepared comprises the potassium salt of the ricinoleic acid ester of 4,4'-AB-4-CPA and the potassium salt of the 11-hydroxyundecanoic acid ester of 4,4'-AB-4-CPA. These compounds functioned as initiator/stabilisers for the emulsion polymerisation of styrene in the absence of conventional surfactant. The yield of polystyrene obtained was above 75%. The stability of the latex is presumably conferred by the dual nature of the molecule; i.e., its hydrophilic/hydrophobic character.

5.8.5. Comparison of the kinetics of emulsion polymerisation of styrene when (i) a water-soluble initiator is used, (ii) an oil-soluble initiator is used, and (iii) the decyl ester of 4,4'-azobis-4-cyanopentanoic acid is used as initiator in the presence of sodium lauryl sulphate. Fig. 5.5 gives the conversion-time curves obtained for the emulsion polymerisation of styrene (55 ml) and water (100 ml) when sodium lauryl sulphate (1 g) is used as colloid stabiliser and (i) potassium persulphate (1.1×10^{-3} mol), (ii) AZBN (1.1×10^{-3} mol), and (iii) the decyl ester of 4,4'-AB-4-CPA (1.1×10^{-3} mol).

All three curves have shapes typical of conversion-time curves for conventional emulsion polymerisation reactions. At the initiator concentrations used, the rate of polymerisation of styrene when the decyl ester of 4,4'-AB-4-CPA is used as initiator is intermediate between the rates of polymerisation obtained with oil-soluble initiators and water-soluble initiators. This is not very surprising, since the decyl ester of 4,4'-AB-4-CPA is partially water-soluble.

5.9. Conclusions drawn from preliminary evaluation. (i) All the derivatives of 4,4'-AB-4-CPA prepared during this project behave as effective initiators for the emulsion polymerisation of styrene in the presence of conventional surfactant. It is therefore inferred that these azo compounds generate free radicals effectively.

Azo compound	Solubility of azo compound		Yield (%) of polymer obtained from attempted surfactant-free emulsion polymerisation of styrene at 70°C using azo compound		Yield (%) of polymer obtained from attempted conventional emulsion polymerisation of styrene at 70°C using sodium lauryl sulphate and azo compound	Yield (%) of polymer obtained from attempted bulk polymerisation of styrene at 70°C using azo compound as initiator
	in water	in styrene	as latex	as bulk polymer		
AZBN	insol	sol	0.51	-----	83.14	20.55
ethyl ester of 4,4'-AB-4-CPA	insol	sol	-----	36.24	80.66	23.42
nonyl ester of 4,4'-AB-4-CPA	part. sol	sol	48.02	47.29	82.41 (latex) 2.43 (solid)	25.64
decyl ester of 4,4'-AB-4-CPA	emulsifies	sol	35.49	-----	85.08	20.33
undecyl ester of 4,4'-AB-4-CPA	part. sol	sol	41.70	53.92	87.91 (latex) 5.53 (solid)	25.19
hexadecyl ester of 4,4'-AB-4-CPA	sol (hot)	sol	14.85	-----	86.85	25.86
octadecyl ester of 4,4'-AB-4-CPA	insol	sol	-----	36.86	86.92	29.83

Table 5.1: Results of polymerisation experiments using azo compounds: AZBN and n-alkyl esters of 4,4'-AB-4-CPA.

Azo compound	Solubility of azo compound		Yield (%) of polymer obtained from attempted surfactant-free emulsion polymerisation of styrene at 70°C using azo compound		Yield (%) of polymer obtained from attempted conventional emulsion polymerisation of styrene at 70°C using sodium lauryl sulphate and azo compound	Yield (%) of polymer obtained from attempted bulk polymerisation of styrene at 70°C using azo compound as initiator
	in water	in styrene	as latex	as bulk polymer		
2-hydroxyethyl ester of 4,4'-AB-4-CPA	sol	insol	-----	19.20	85.97	12.60
trimethylol propane ester of 4,4'-AB-4-CPA	sol (hot)	insol	4.42	40.66	88.95	13.92
pentaerythritol ester of 4,4'-AB-4-CPA	insol	sol	5.94	-----	80.68	35.00

Table 5.2: Results of polymerisation experiments using azo compounds: hydroxyalkyl esters of 4,4'-AB-4-CPA.

Azo compound	Solubility of azo compound		Yield (%) of polymer obtained from attempted surfactant-free emulsion polymerisation of styrene at 70°C using azo compound		Yield (%) of polymer obtained from attempted conventional emulsion polymerisation of styrene at 70°C using sodium lauryl sulphate and azo compound	Yield (%) of polymer obtained from attempted bulk polymerisation of styrene at 70°C using azo compound as initiator
	in water	in styrene	as latex	as bulk polymer		
cyclohexyl ester of 4,4'-AB-4-CPA	insol	sol	-----	41.28	not carried out	not carried out
phenyl ester of 4,4'-AB-4-CPA	sol (hot)	sol	-----	35.58	82.21	14.14
resorcinol ester of 4,4'-AB-4-CPA	sol (hot)	insol	-----	12.95	88.68	13.92
phloroglucinol ester of 4,4'-AB-4-CPA	insol	insol	-----	10.34	84.64	2.21
o-hydroxybenzoic acid ester of 4,4'-AB-4-CPA	insol	insol	-----	25.28	81.19	11.00
p-hydroxybenzoic acid ester of 4,4'-AB-4-CPA	insol	insol	-----	13.15	83.36	3.31
potassium salt of o-hydroxybenzoic acid ester of 4,4'-AB-4-CPA	insol	insol	-----	40.91	83.38	17.02
potassium salt of p-hydroxybenzoic acid ester of 4,4'-AB-4-CPA	insol	insol	-----	6.50	85.39	21.33

Table 5.3: Results of polymerisation experiments using azo compounds: alicyclic and aromatic esters of 4,4'-AB-4-CPA.

Azo compound	Solubility of azo compound		Yield (%) of polymer obtained from attempted surfactant-free emulsion polymerisation of styrene at 70°C using azo compound		Yield (%) of polymer obtained from attempted conventional emulsion polymerisation of styrene at 70°C using sodium lauryl sulphate and azo compound	Yield (%) of polymer obtained from attempted bulk polymerisation of styrene at 70°C using azo compound as initiator
	in water	in styrene	as latex	as bulk polymer		
decyl amide of 4,4'-AB-4-CPA	insol	sol (hot)	-----	30.63	88.95	33.92
dodecyl amide of 4,4'-AB-4-CPA	insol	sol (hot)	-----	14.36	79.47	28.29
tetradecyl amide of 4,4'-AB-4-CPA	insol	sol (hot)	-----	30.50	75.09	19.89
decyl amine salt of 4,4'-AB-4-CPA	sol	sol (hot)	-----	31.54	89.70	6.85

Table 5.4: Results of polymerisation experiments using azo compounds: amides and amine salts of 4,4'-AB-4-CPA.

Azo compound	Solubility of azo compound		Yield (%) of polymer obtained from attempted surfactant-free emulsion polymerisation of styrene at 70°C using azo compound		Yield (%) of polymer obtained from attempted conventional emulsion polymerisation of styrene at 70°C using sodium lauryl sulphate and azo compound	Yield (%) of polymer obtained from attempted bulk polymerisation of styrene at 70°C using azo compound as initiator
	in water	in styrene	as latex	as bulk polymer		
ricinoleic acid ester of 4,4'-AB-4-CPA	insol	sol	-----	33.10	87.42	15.80
potassium salt of ricinoleic acid ester of 4,4'-AB-4-CPA	sol	insol	74.03	-----	85.52	not carried out
potassium salt of 11-hydroxy-undecanoic acid ester of 4,4'-AB-4-CPA	sol	insol	81.33	-----	not carried out	not carried out

Table 5.5: Results of polymerisation experiments using azo compounds: hydroxy acid esters of 4,4'-AB-4-CPA and their potassium salts.

Azo compound	Yield (%) of polymer obtained from attempted surfactant-free emulsion polymerisation of styrene at 70°C using azo compound		Yield (%) of polymer obtained from attempted conventional emulsion polymerisation of styrene at 70°C using sodium lauryl sulphate and azo compound	Yield (%) of polymer obtained from attempted bulk polymerisation of styrene at 70°C using azo compound as initiator	
	0.011 mol azo	2.25 g azo		0.011 mol azo	2.25 g azo
$FA(EO)_2Es$ of 4,4'-AB-4-CPA	17.06	34.34	86.41	34.70	54.58
$FA(EO)_6Es$ of 4,4'-AB-4-CPA	22.67	29.70	87.43	30.50	45.52
$FA(EO)_{10}Es$ of 4,4'-AB-4-CPA	14.39	26.52	83.87	27.84	32.93
$FA(EO)_{14}Es$ of 4,4'-AB-4-CPA	16.44	22.28	85.90	26.74	31.16
$FA(EO)_{24}Es$ of 4,4'-AB-4-CPA	7.73 + 65.86 solid	17.68 + 54.36 solid	86.41	27.62	23.12
$FA(EO)_{30}Es$ of 4,4'-AB-4-CPA	27.05	22.36	87.93	25.64	20.77
$FA(EO)_{45}Es$ of 4,4'-AB-4-CPA	12.15	9.55	86.92	24.97	18.56
$FA(EO)_{60}Es$ of 4,4'-AB-4-CPA	21.08	36.18	81.70	30.28	6.63

Table 5.6: Results of polymerisation experiments using azo compounds: fatty-alcohol ethoxylate esters of 4,4'-AB-4-CPA.

FA(EO)	Solubility of FA(EO) (70°C)		Solubility of FA(EO)Es (70°C)		Solubility of FA(EO) (room temperature)		Solubility of FA(EO)Es (room temperature)	
	water	styrene	water	styrene	water	styrene	water	styrene
$FA(EO)_2$	sparingly soluble white dispersion cloudy	sol	sparingly soluble white dispersion cloudy	sol	sparingly soluble white dispersion cloudy	sol	sparingly soluble	sol
$FA(EO)_6$	turbid solution	sol	sparingly soluble white dispersion cloudy	sol	sparingly soluble	sol	sparingly soluble	sol
$FA(EO)_{10}$	slight cloudiness sol	sol	less sol than at room temp; sparingly soluble white dispersion	sol	sparingly soluble	sol	white dispersion cloudy	sol
$FA(EO)_{14}$	sol	sol	turns much more cloudy at 70°C	sol	sparingly soluble	sol	white dispersion cloudy	sol
$FA(EO)_{24}$	sol	sol	turns cloudy at 70°C	sol	sol slight cloudiness	sol	sol slight cloudiness	sol
$FA(EO)_{30}$	sol	sol	sol	sol	sol	sol	sol	sol
$FA(EO)_{45}$	sol	sol	sol	sol	sol	sol	sol	sol
$FA(EO)_{60}$	sol	sol	sol	sol	sol	sol	sol	sol

Table 5.7: Solubilities of fatty-alcohol ethoxylates and of their 4,4'-AB-4-CPA esters in water and in styrene.

Azo compound	Sodium lauryl sulphate	Yield (%) of polymer	Polystyrene particle size (nm)	Particle number N (cm^{-3})	Surface tension of latex ($mN\ m^{-1}$)
AZBN	absent	0.51	235	4.81×10^{11}	not measured
	present	83.14	94.4	7.57×10^{14}	not measured
ethyl ester of 4,4'-AB-4-CPA	absent	-----	-----	-----	not measured
	present	80.66	64.5	2.37×10^{15}	not measured
nonyl ester of 4,4'-AB-4-CPA	absent	48.02	127	1.95×10^{14}	55.87
	present	82.41	67.3	1.97×10^{15}	56.70
decyl ester of 4,4'-AB-4-CPA	absent	35.49	126	1.33×10^{14}	67.40
	present	35.08	67.2	2.10×10^{15}	not measured
undecyl ester of 4,4'-AB-4-CPA	absent	41.70	112	2.85×10^{14}	65.20
	present	87.94	98.4	6.49×10^{14}	61.00
hexadecyl ester of 4,4'-AB-4-CPA	absent	14.85	126	5.09×10^{13}	73.85
	present	86.85	64.5	2.30×10^{15}	53.20
octadecyl ester of 4,4'-AB-4-CPA	absent	-----	-----	-----	not measured
	present	86.92	58.7	3.06×10^{15}	not measured

Table 5.8: Results of characterisation of polystyrene latices obtained using azo initiators: AZBN and n-alkyl esters of 4,4'-AB-4-CPA.

Azo compound	Sodium lauryl sulphate	Yield (%) of polymer	Polystyrene particle size (nm)	Particle number N (cm^{-3})	Surface tension of latex ($mN\ m^{-1}$)
2-hydroxyethyl ester of 4,4'-AB-4-CPA	absent	-----	-----	-----	not measured
	present	85.97	70.4	1.77×10^{15}	not measured
trimethylol ester of 4,4'-AB-4-CPA	absent	4.42	891	3.86×10^{11}	not measured
	present	88.95	61.5	2.71×10^{15}	not measured
pentaerythritol ester of 4,4'-AB-4-CPA	absent	5.94	-----	-----	not measured
	present	80.68	-----	-----	not measured

Table 5.9: Results of characterisation of polystyrene latices obtained using azo initiators: hydroxyalkyl esters of 4,4'-AB-4-CPA.

Azo compound	Sodium lauryl sulphate	Yield (%) of polymer	Polystyrene particle size (nm)	Particle number N (cm^{-3})	Surface tension of latex ($mN\ m^{-1}$)
cyclohexyl ester of 4,4'-AB-4-CPA	absent present	----- not recorded	----- -----	----- -----	not measured not measured
phenyl ester of 4,4'-AB-4-CPA	absent present	----- 82.21	----- 59.5	----- 2.93×10^{15}	not measured not measured
resorcinol ester of 4,4'-AB-4-CPA	absent present	----- 88.68	----- 75.0	----- 1.08×10^{15}	not measured not measured
phloroglucinol ester of 4,4'-AB-4-CPA	absent present	----- 84.64	----- 75.8	----- 1.42×10^{15}	not measured not measured
o-hydroxybenzoic acid ester of 4,4'-AB-4-CPA	absent present	----- 81.19	----- -----	----- -----	not measured not measured
p-hydroxybenzoic acid ester of 4,4'-AB-4-CPA	absent present	----- 83.36	----- 78.8	----- 1.22×10^{15}	not measured not measured
potassium salt of o-hydroxybenzoic acid ester of 4,4'-AB-4-CPA	absent present	----- 83.38	----- 61.7	----- 2.87×10^{15}	not measured not measured
potassium salt of p-hydroxybenzoic acid ester of 4,4'AB-4-CPA	absent present	----- 85.39	----- 73.3	----- 1.57×10^{15}	not measured not measured

Table 5.10: Results of characterisation of polystyrene latices using azo initiators: acyclic and aromatic esters of 4,4'-AB-4-CPA.

Azo compound	Sodium lauryl sulphate	Yield (%) of polymer	Polystyrene particle size (nm)	Particle number N (cm^{-3})	Surface tension of latex ($mN\ m^{-1}$)
decyl amide of 4,4'-AB-4-CPA	absent	-----	-----	-----	not measured
	present	88.95	93.3	7.84×10^{14}	not measured
dodecyl amide of 4,4'-AB-4-CPA	absent	-----	-----	-----	not measured
	present	79.47	112	4.02×10^{14}	not measured
tetradecyl amide of 4,4'-AB-4-CPA	absent	-----	-----	-----	not measured
	present	75.09	86.2	8.24×10^{14}	not measured
decylamine salt of 4,4'-AB-4-CPA	absent	31.54	not measured	not measured	not measured
	present	89.70	84.3	1.03×10^{15}	not measured

Table 5.11: Results of characterisation of polystyrene latices using azo initiators: amides and amine salts of 4,4'-AB-4-CPA.

Azo compound	Sodium lauryl sulphate	Yield (%) of polymer	Polystyrene particle size (nm)	Particle number N (cm^{-3})	Surface tension of latex ($mN\ m^{-1}$)
potassium salt of ricinoleic acid ester of 4,4'-AB-4-CPA	absent	74.03	65.3	2.16×10^{15}	45.85
	present	85.52	65.3	2.16×10^{15}	60.50
potassium salt of 11-hydroxy-undecanoic acid ester of 4,4'-AB-4-CPA	absent	81.83	62.8	2.36×10^{15}	53.85
	present	not measured	not measured	not measured	not measured

Table 5.12: Results of characterisation of polystyrene latices using azo initiators: potassium salts of hydroxy acid esters of 4,4'-AB-4-CPA.

Azo compound (0.011 mol)	Sodium lauryl sulphate	Yield (%) of polymer	Polystyrene particle size (nm)	Particle number N (cm^{-3})	Surface tension of latex ($mN\ m^{-1}$)
$FA(EO)_2Es$ of 4,4'-AB-4-CPA	absent	17.06	145	3.82×10^{13}	not measured
	present	86.41	82.1	1.12×10^{15}	not measured
$FA(EO)_6Es$ of 4,4'-AB-4-CPA	absent	22.67	173	3.09×10^{13}	not measured
	present	87.43	69.4	1.85×10^{15}	not measured
$FA(EO)_{10}Es$ of 4,4'-AB-4-CPA	absent	14.39	184	1.81×10^{13}	not measured
	present	83.87	84.3	1.00×10^{15}	not measured
$FA(EO)_{14}Es$ of 4,4'-AB-4-CPA	absent	16.44	167	2.41×10^{13}	not measured
	present	85.90	85.4	9.93×10^{14}	not measured
$FA(EO)_{24}Es$ of 4,4'-AB-4-CPA	absent	7.73	174	2.35×10^{13}	not measured
	present	86.41	98.0	6.57×10^{14}	not measured
$FA(EO)_{30}Es$ of 4,4'-AB-4-CPA	absent	27.05	470	1.79×10^{12}	not measured
	present	87.93	78.8	1.30×10^{15}	not measured
$FA(EO)_{45}Es$ of 4,4'-AB-4-CPA	absent	12.15	222	7.32×10^{12}	not measured
	present	86.92	110	4.65×10^{14}	not measured
$FA(EO)_{60}Es$ of 4,4'-AB-4-CPA	absent	21.08	117	3.64×10^{14}	56.50
	present	81.70	85.3	9.68×10^{14}	not measured

Table 5.13a: Results of characterisation of polystyrene latices using azo initiators: fatty-alcohol ethoxylate esters of 4,4'-AB-4-CPA.

Azo compound (2.25 g)	Sodium lauryl sulphate	Yield (%) of polymer	Polystyrene particle size (nm)	Particle number N (cm^{-3})	Surface tension of latex ($mN\ m^{-1}$)
$FA(EO)_2Es$ of 4,4'-AB-4-CPA	absent	34.34	139	1.00×10^{14}	not measured
$FA(EO)_6Es$ of 4,4'-AB-4-CPA	absent	29.70	137	7.93×10^{13}	not measured
$FA(EO)_{10}Es$ of 4,4'-AB-4-CPA	absent	26.52	173	3.51×10^{13}	not measured
$FA(EO)_{14}Es$ of 4,4'-AB-4-CPA	absent	22.28	171	3.04×10^{13}	not measured
$FA(EO)_{24}Es$ of 4,4'-AB-4-CPA	absent	17.68	136	1.15×10^{14}	not measured
$FA(EO)_{30}$ of 4,4'-AB-4-CPA	absent	22.36	493	1.34×10^{12}	not measured
$FA(EO)_{45}Es$ of 4,4'-AB-4-CPA	absent	9.55	368	1.31×10^{12}	not measured
$FA(EO)_{60}Es$ of 4,4'-AB-4-CPA	absent	36.18	174	4.49×10^{13}	not measured

Table 5.13b: Results of characterisation of polystyrene latices using azo initiators: fatty-alcohol ethoxylate esters of 4,4'-AB-4-CPA.

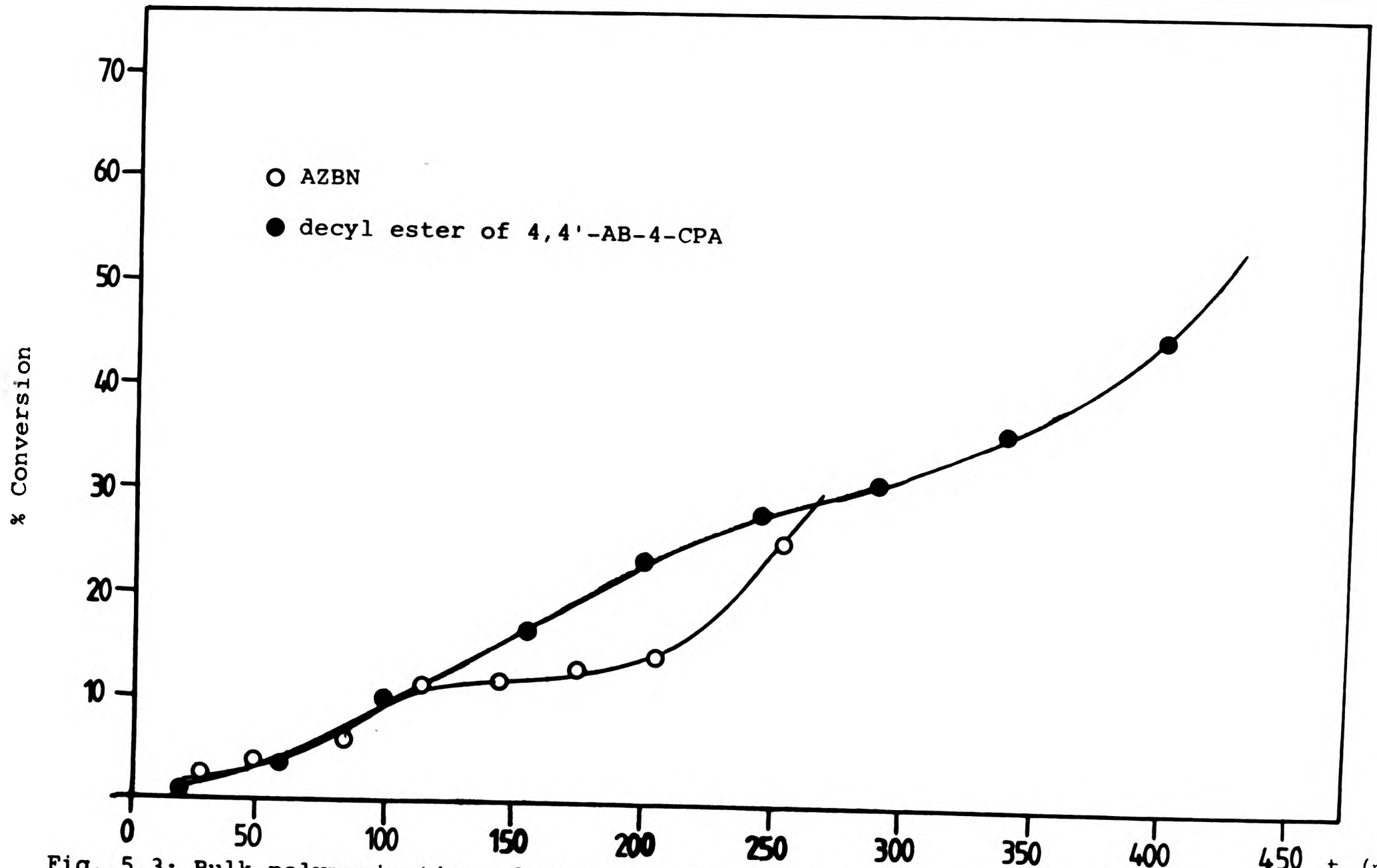


Fig. 5.3: Bulk polymerisation of styrene using (1) AZBN and (2) the decyl ester of 4,4'-AB-4-CPA as initiators.

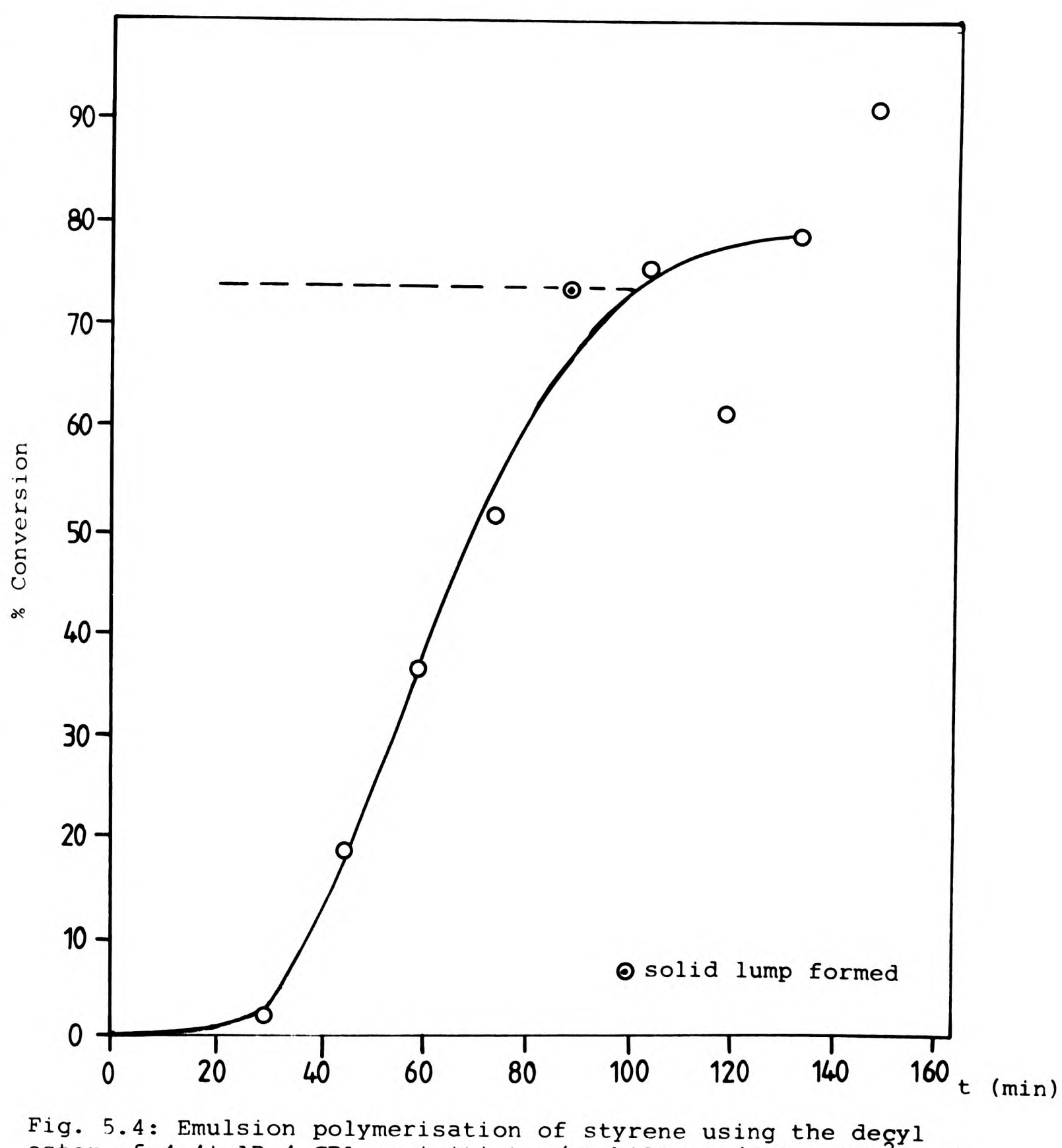


Fig. 5.4: Emulsion polymerisation of styrene using the decyl ester of 4,4'-AB-4-CPA as initiator/stabiliser (1.1×10^{-2} mol) with a styrene:water volume ratio of 50:100 at 52°C.

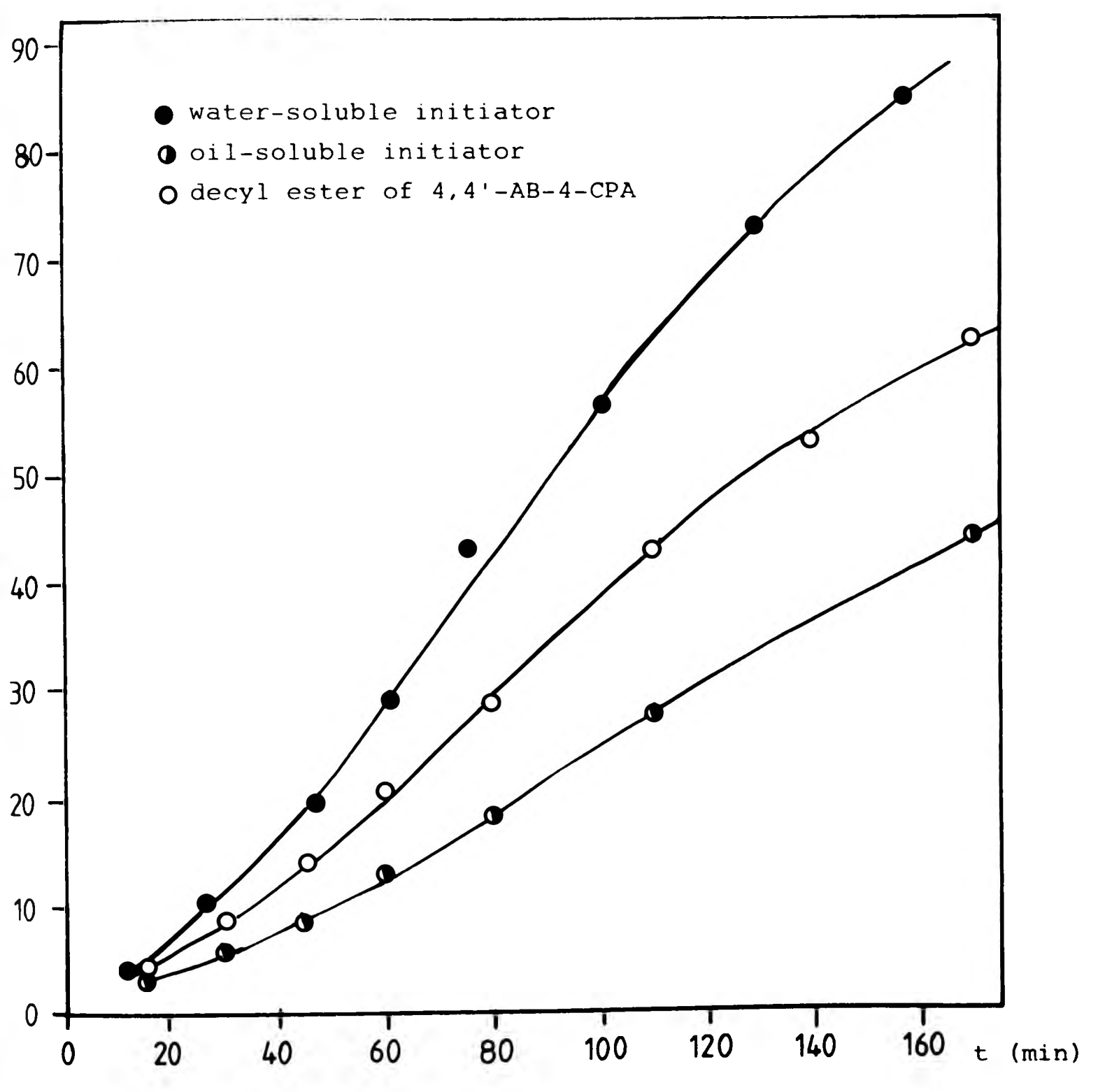


Fig. 5.5: Comparison of the kinetics of emulsion polymerisation of styrene when (i) a water-soluble initiator is used, (ii) an oil-soluble initiator is used, and (iii) the decyl ester of 4,4'-AB-4-CPA is used in the presence of sodium lauryl sulphate.

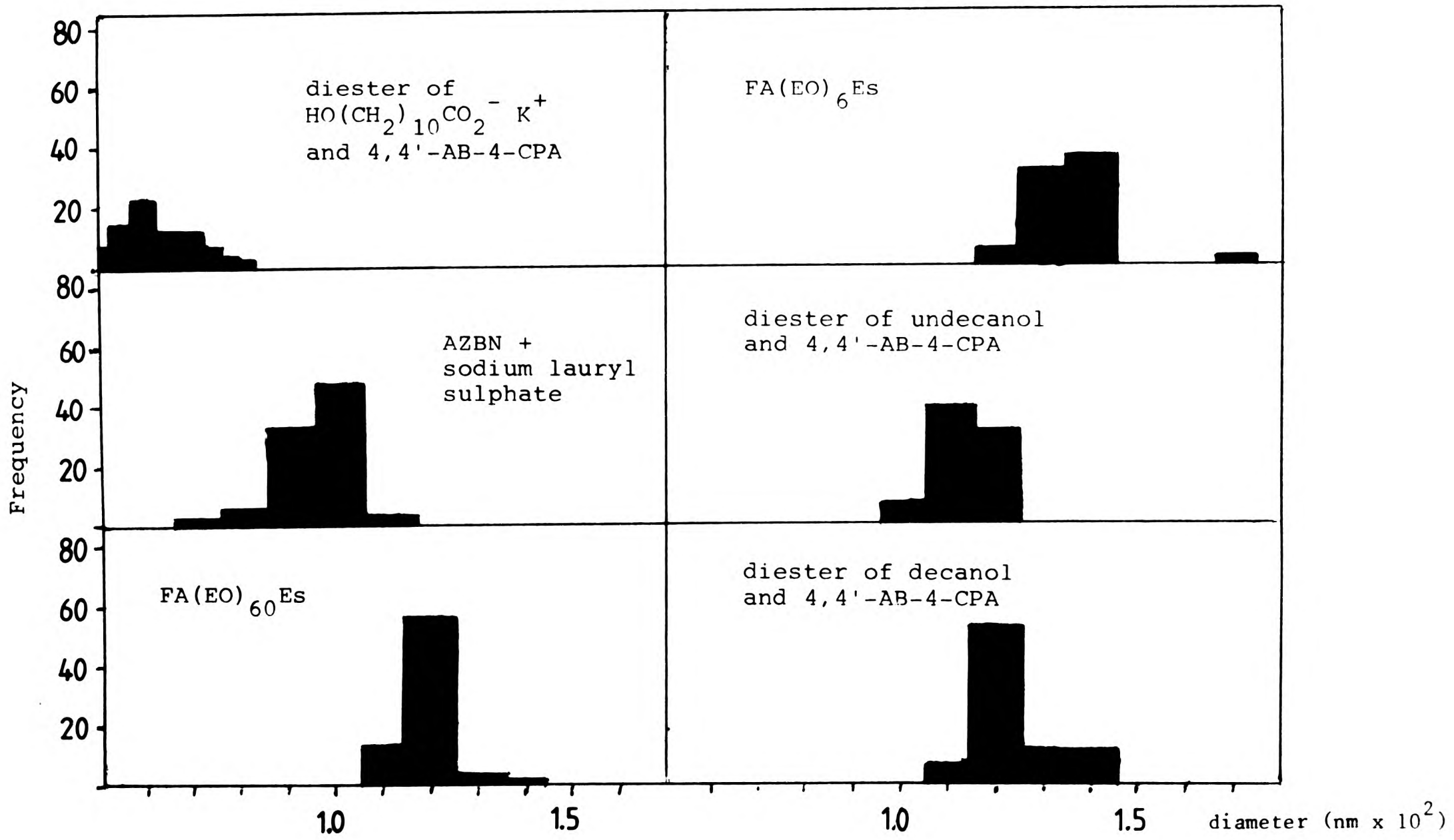


Fig. 5.6: Particle-size distribution of latices produced in the emulsion polymerisation of styrene using various initiator/stabiliser systems.

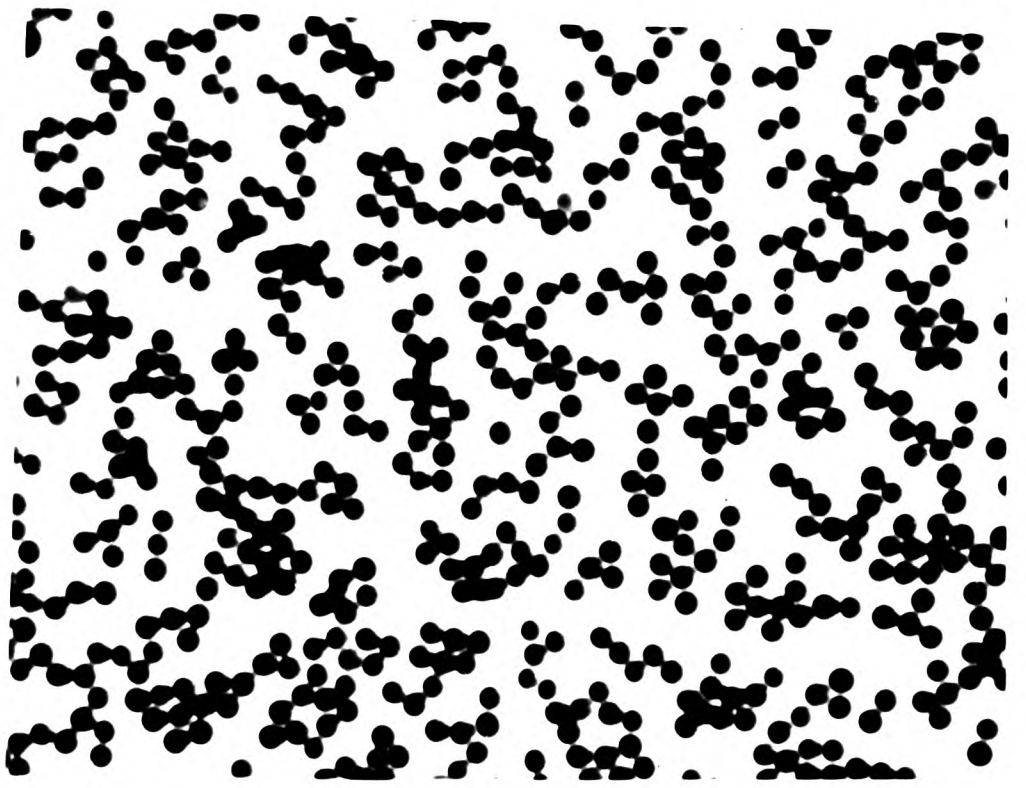


Fig. 5.7a: Electron micrograph of latex obtained using the undecyl ester of 4,4'-azobis-4-cyanopentanoic acid as initiator/stabiliser.

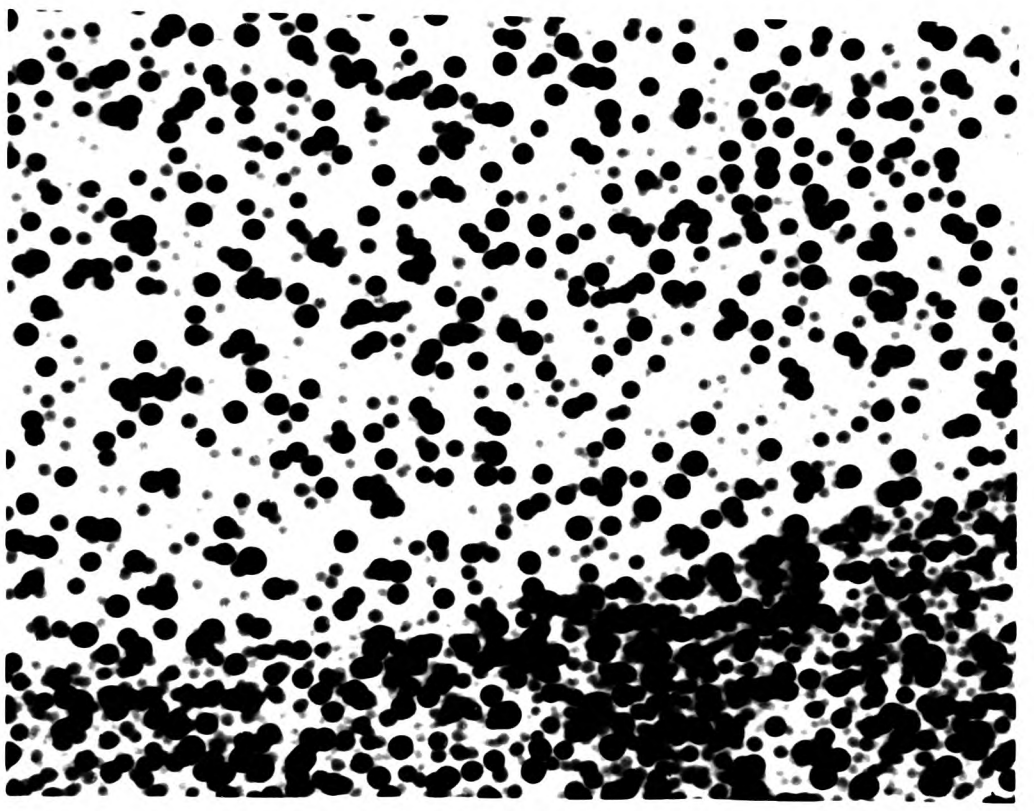


Fig. 5.7b: Electron micrograph of latex obtained using the undecyl ester of 4,4'-azobis-4-cyanopentanoic acid as initiator and sodium lauryl sulphate as stabiliser.

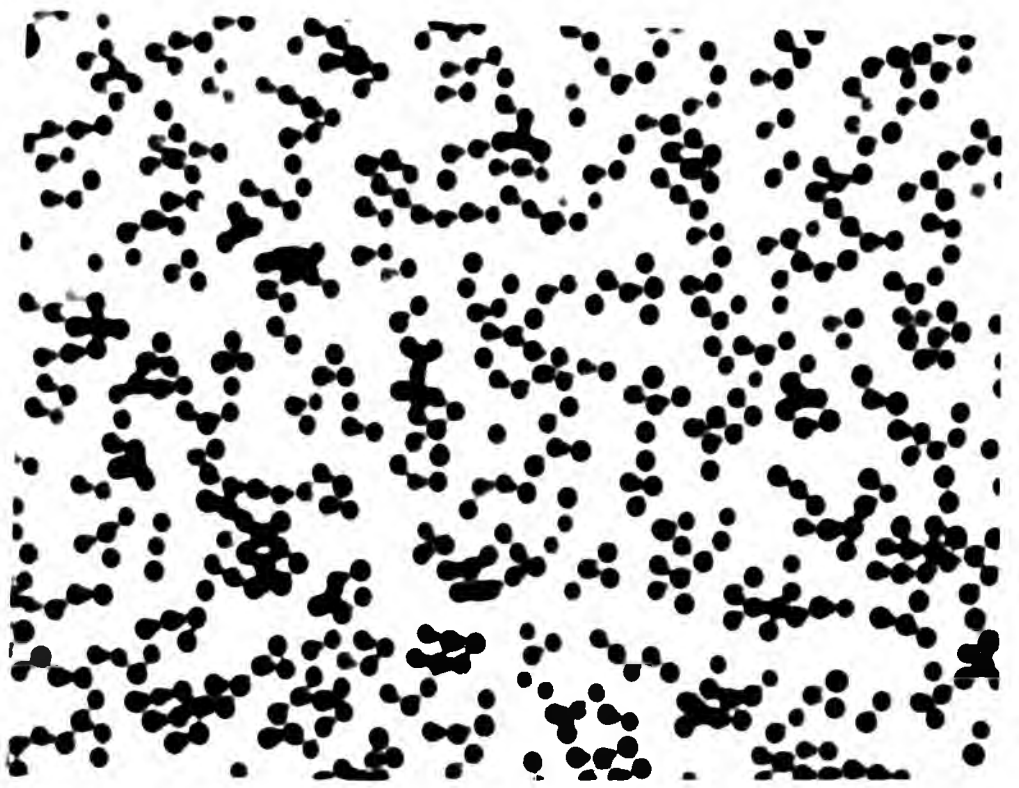


Fig. 5.7a: Electron micrograph of latex obtained using the undecyl ester of 4,4'-azobis-4-cyanopentanoic acid as initiator/stabiliser.

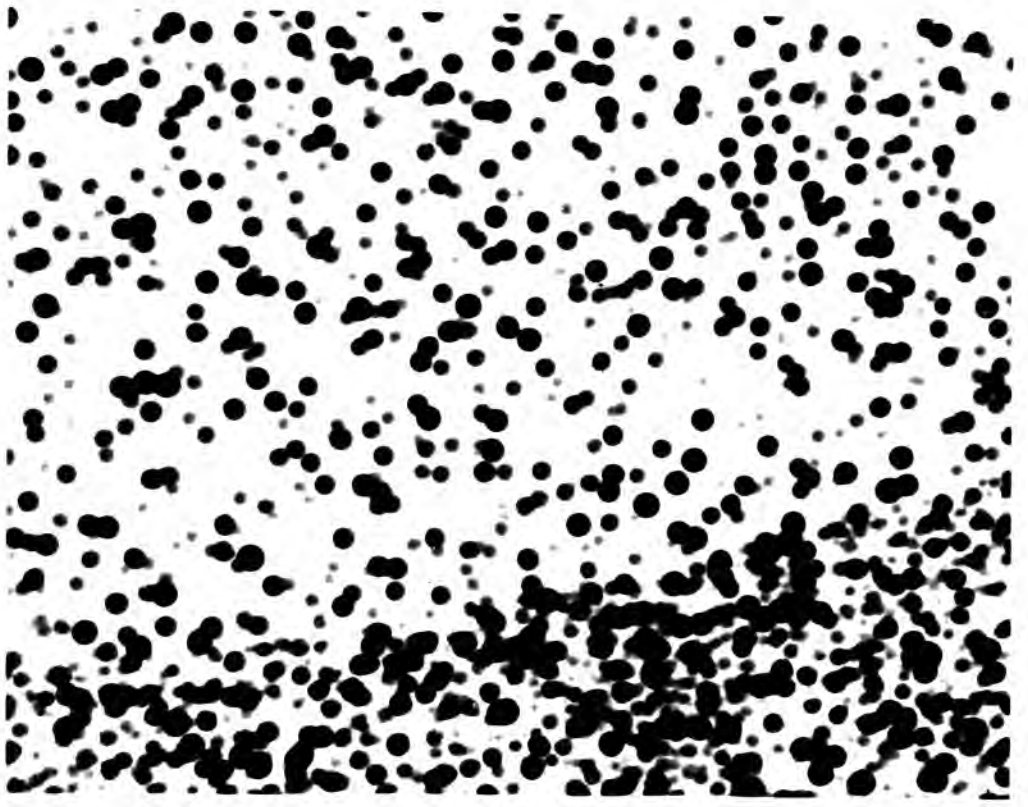


Fig. 5.7b: Electron micrograph of latex obtained using the undecyl ester of 4,4'-azobis-4-cyanopentanoic acid as initiator and sodium lauryl sulphate as stabiliser.

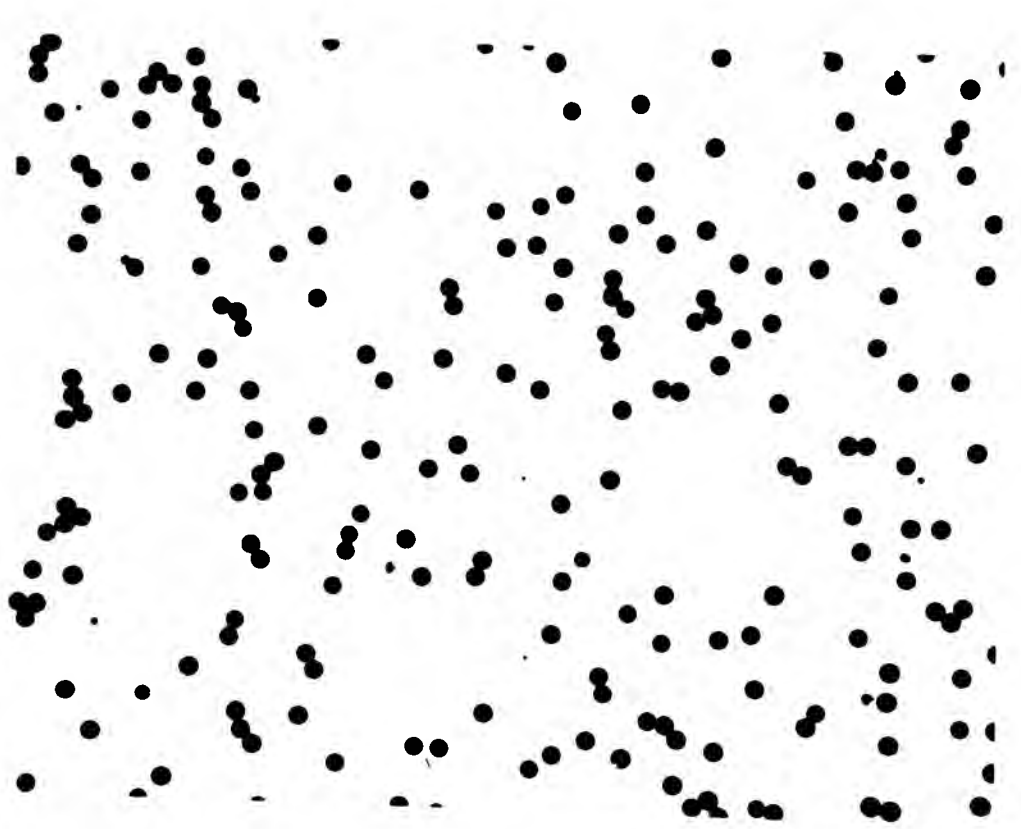


Fig. 5.7c: Electron micrograph of latex obtained using the hexadecyl ester of 4,4'-azobis-4-cyanopentanoic acid as initiator/stabiliser.

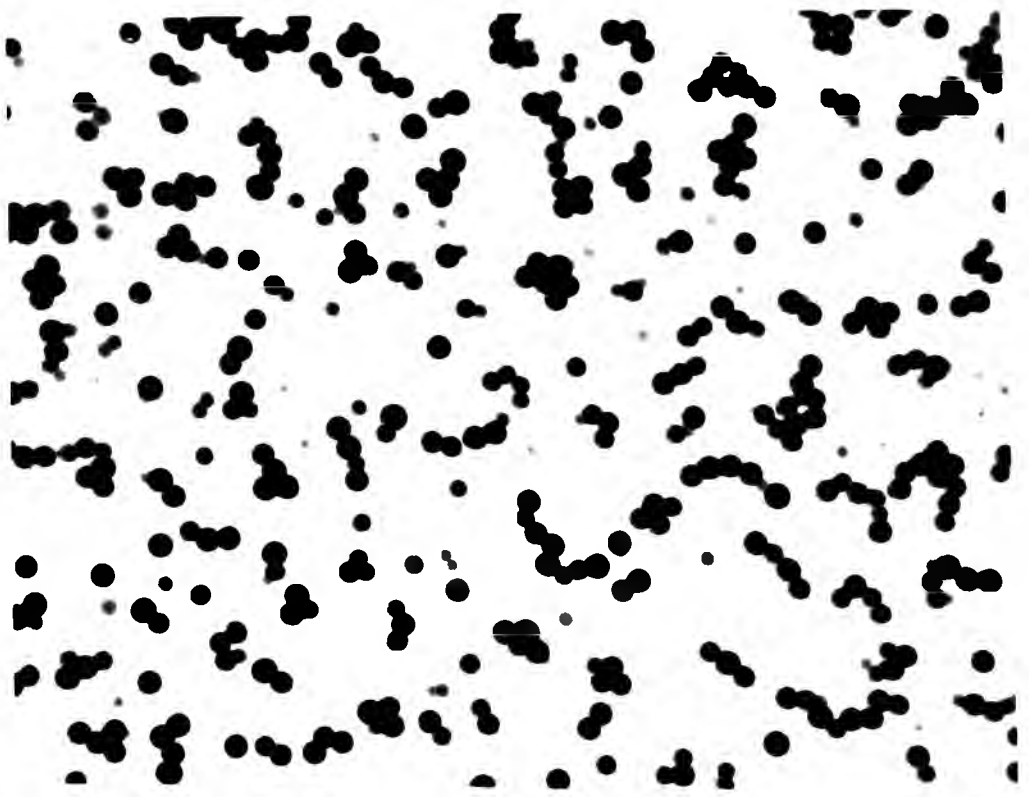


Fig. 5.7d: Electron micrograph of latex obtained using AZBN as initiator and sodium lauryl sulphate as stabiliser.

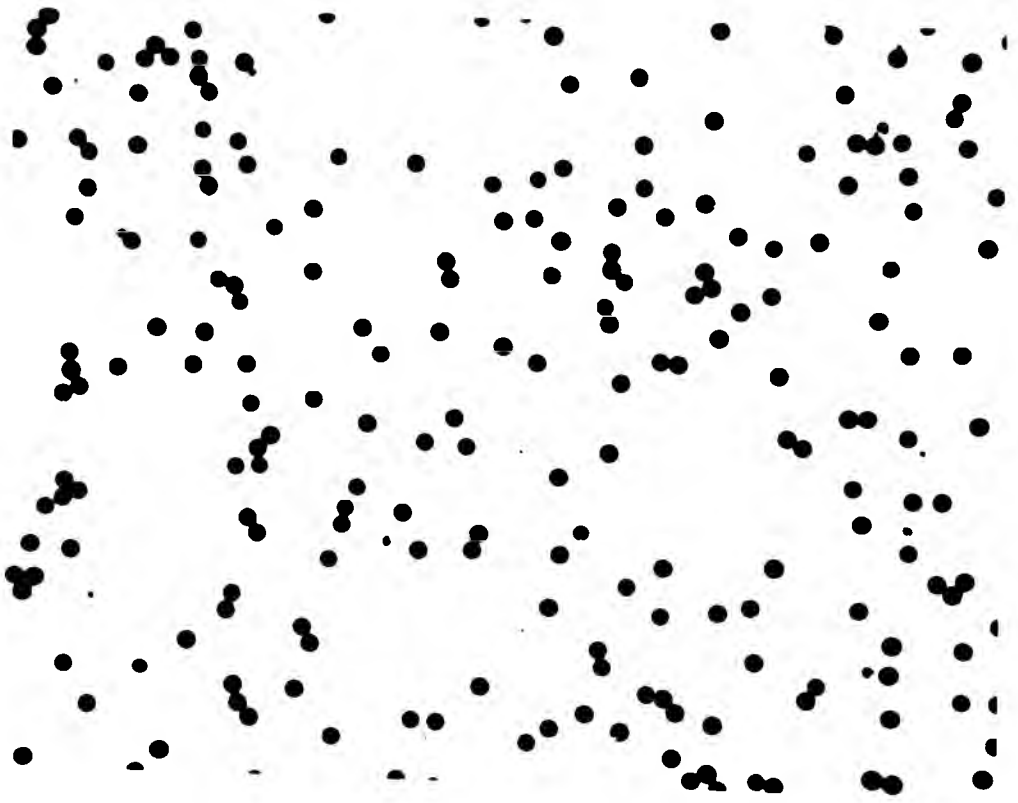


Fig. 5.7c: Electron micrograph of latex obtained using the hexadecyl ester of 4,4'-azobis-4-cyanopentanoic acid as initiator/stabiliser.

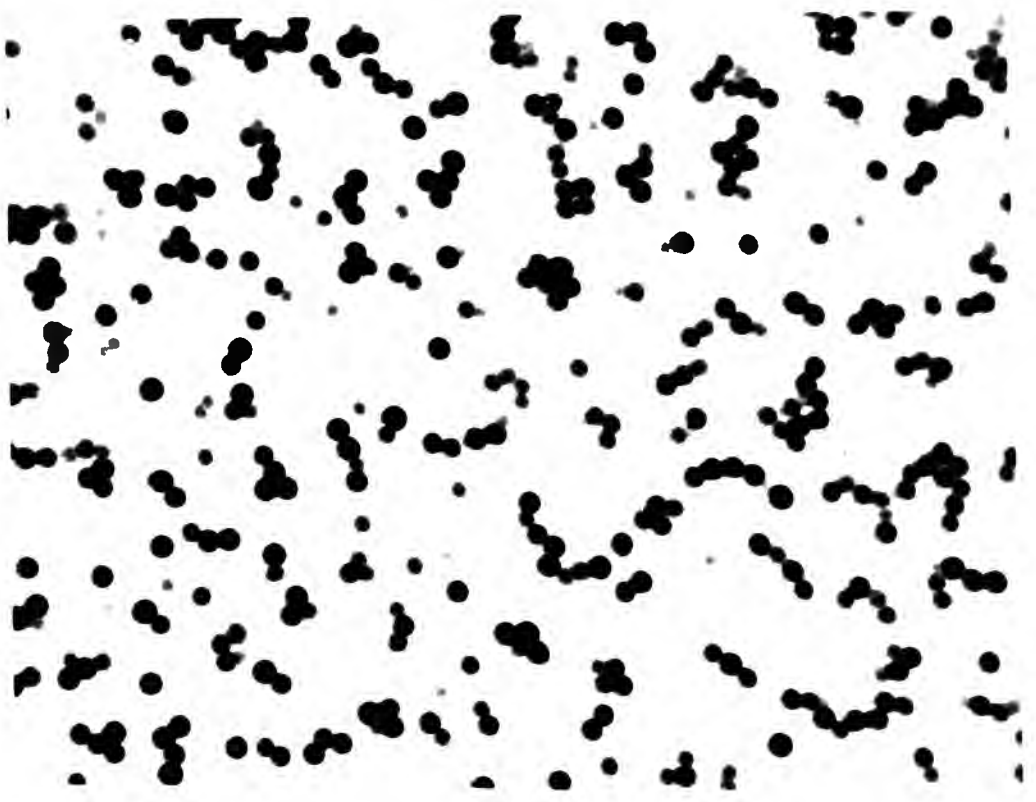


Fig. 5.7d: Electron micrograph of latex obtained using AZBN as initiator and sodium lauryl sulphate as stabiliser.

(ii) Almost all of the derivatives behave as effective initiators for the bulk polymerisation of styrene. It is believed that the failure of a few compounds to initiate the polymerisation of styrene in bulk satisfactorily is due to their low solubility in styrene, and not to any inability to generate free radicals effectively.

(iii) Some of the compounds prepared behave as initiators for emulsion polymerisation in the absence of conventional surfactant. Thus, these compounds appear to be capable of performing the dual functions of polymerisation initiator and colloidal stabiliser.

5.10. A problem: An apparent change in the behaviour of the straight-chain alkyl esters of 4,4'-azobis-4-cyanopentanoic acid.

5.10.1. Introduction. For a period of approximately thirteen months during this project, some of the esters of straight-chain alcohols and 4,4'-AB-4-CPA acted as both initiators and stabilisers for the emulsion polymerisation of styrene in the absence of conventional surfactant, yielding very stable and monodisperse latices. However, suddenly esters prepared similarly to those that had previously showed such unexpected behaviour failed to yield polystyrene latices when used as initiator/stabilisers for the emulsion polymerisation of styrene in the absence of conventional surfactant. The infrared spectra of these esters seemed to be identical to those of the products obtained during the previous work, but the newly-prepared esters were now colourless and did not have the typical odour of an ester. Furthermore, their solubility in water, cold or warm, was practically nil. This, of course, is what one would expect from a compound such as the decyl ester of 4,4'-AB-4-CPA, and not the partial solubility in water which had been observed in the case of the compounds previously believed to have been these esters. The infrared spectrum of the acid chloride from which this different ester was prepared was observed to be very different to the infrared spectrum of the acid chloride obtained previously. The most marked differences (see Fig. 5.8) were the absence of a second carbonyl peak and the absence of a large OH-like band present in the original acid chloride. Thus it seems possible that 4,4'-AB-4-CPC can exist in two forms. The original acid chloride has been designated as I and the subsequent acid chloride as II.

4,4'-AB-4-CPC with an infrared spectrum resembling that of I has also been prepared by two other workers, Roca[161] and Jinanwa[162].

Table 5.14 shows the most marked differences between the two acid chlorides and the esters prepared from them. Fig. 5.8 shows the infrared spectra of acid chlorides I and II.

	acid chloride	
	I	II
infrared spectrum of acid chloride	two carbonyl peaks at 1800 cm^{-1}, 1750 cm^{-1} OH-like band at 3000 cm^{-1}	one carbonyl peak at 1800 cm^{-1}; no OH-like band present
melting point of acid chloride	92-94°C	74-76°C
product of reaction of acid chloride with two mol of alcohol	ester (according to infrared spectrum)	ester (according to infrared spectrum)
infrared spectrum of ester	one carbonyl peak at 1800 cm^{-1}; no OH band present	one carbonyl peak at 1800 cm^{-1}; no OH band present
appearance of ester	yellow wax	white wax
smell of ester	typical ester odour	odourless
result of attempted emulsion polymerisation of styrene using ester as initiator/stabiliser in absence of conventional surfactant	stable latex	no reaction

Table 5.14. Characteristics of the two acid chlorides obtained from 4,4'-AB-4-CPA and of the esters prepared from them.

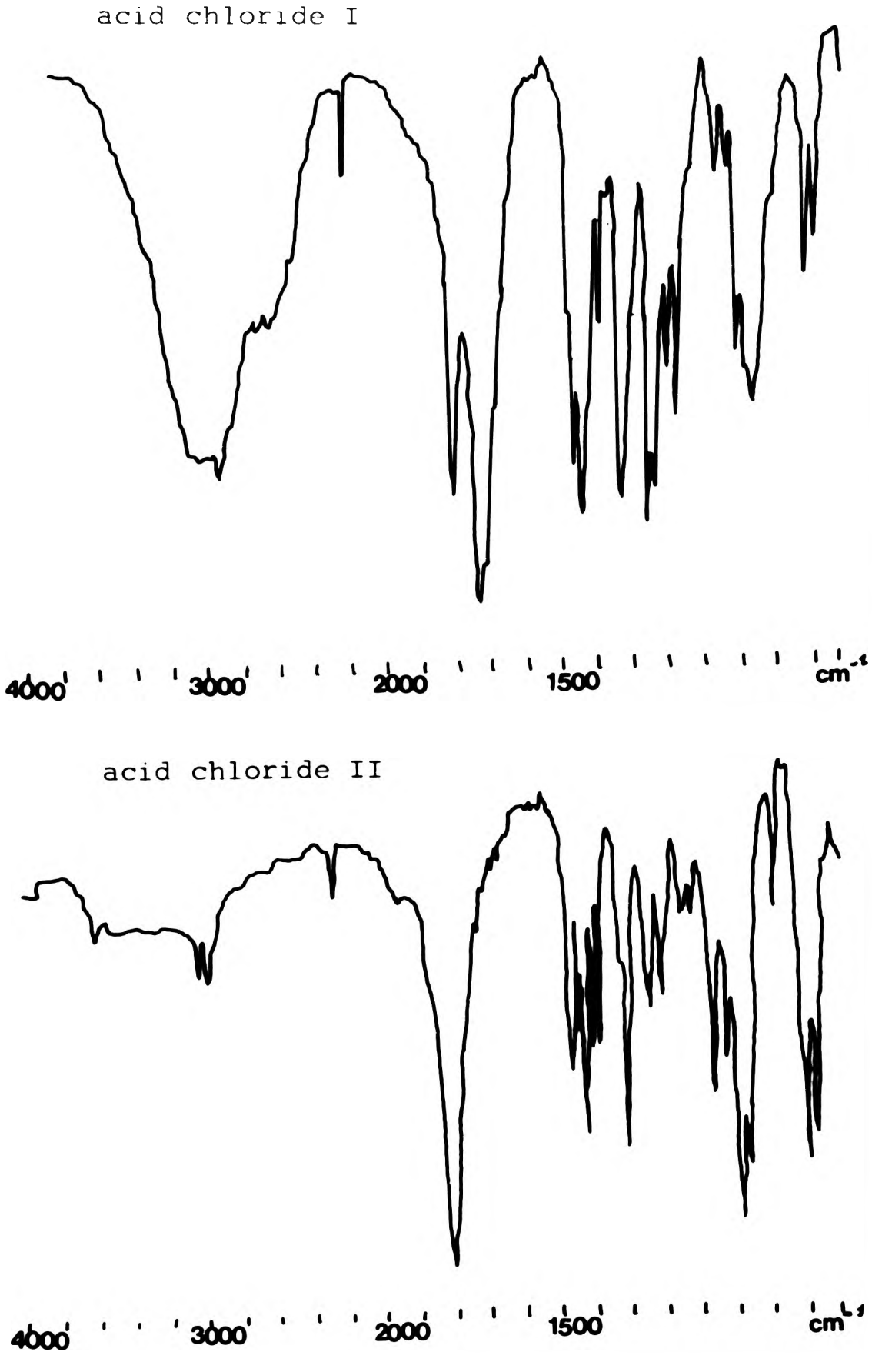


Fig. 5.8: Infrared spectra of acid chloride I and acid chloride II.

Since the esters derived from acid chloride I gave stable, monodisperse latices when used as initiator/stabilisers in the emulsion polymerisation of styrene in the absence of conventional surfactant, and since the esters derived from acid chloride II fail to do so, a considerable effort was made to try to prepare acid chloride I again and to understand why apparently identical preparative procedures gave two types of acid chloride and two series of esters derived from the acid chlorides.

5.10.2. Attempts at preparing 4,4'-azobis-4-cyanopentanoyl chloride I. The first step taken in an attempt to solve the problem was to use a new batch of 4,4'-AB-4-CPA from Aldrich. When this acid did not give the original acid chloride, a new batch of phosphorus pentachloride was used. Repeating the preparation and using pure "Analar" reagents still produced acid chloride II. Further attempts at preparation using 4,4'-AB-4-CPA from Sigma and acid prepared by the writer met with the same result, namely, the production of acid chloride II.

The reagents supplied by Aldrich were characterised as far as possible to confirm their identity. The acids, both that from Aldrich and that prepared by the writer, were extensively characterised, using melting points, infrared spectra, ^{13}C NMR spectra, elemental analysis, ultraviolet spectra and acid-group analysis. All the evidence pointed to all the samples being 4,4'-AB-4-CPA.

5.10.3. Supplementary experiments.

5.10.3.1. Chlorine determination by the oxygen-flask method. A capsule containing an accurately-known weight of acid chloride II was placed in the cage of the oxygen flask together with a fuse of ashless filter paper. A few pellets of KOH were placed in a clean flask and distilled water was added. The flask was flushed with oxygen for about four minutes and then stoppered. The fuse was lit and immersed in the flask quickly. The flask was allowed to stand until all the "fog" inside had settled. The solution was transferred to a beaker, and washed thoroughly with distilled water. The washing was repeated three times. A few drops of methyl red were added to the solution, which was carefully acidified with concentrated nitric acid. Distilled water was added. The contents of the beaker were

then stirred vigorously and titrated against 0.098 M aqueous silver nitrate solution. The chlorine content found in acid chloride II by this method corresponded to approximately 1.7 atoms per molecule.

5.10.3.2. Chlorine determination by the Volhard method. Acid chloride II (1 g) was dissolved in a solution of alcoholic KOH. It was then acidified with concentrated nitric acid and titrated with 0.098 M aqueous silver nitrate solution. The volume of silver nitrate solution used was 72.9 ml, and the excess was back titrated with 0.05 M aqueous ammonium thiocyanate solution. The indicator used was ferric alum. The chlorine content found in acid chloride II by this method corresponded to approximately 1.95 atoms per molecule.

5.10.3.3. Chlorine determination using a gravimetric method. Acid chloride I (1 g) was treated with methanolic NaOH until the solution was alkaline to pH paper. The solution was then made acidic to pH paper with nitric acid. A white solid precipitated, which was presumed to be 4,4'-AB-4-CPA. The solution was decanted and the solid was washed with methanol. Aqueous silver nitrate solution was added to the solution. A white precipitate formed, presumably silver chloride. The chlorine content found in acid chloride I by this method corresponded to approximately 1.7 atoms per molecule.

5.10.3.4. Synthesis of 2,4-dinitrophenylhydrazone of laevulinic acid. The laevulinic acid used by the writer for the preparation of 4,4'-AB-4-CPA was characterised to confirm its identity. A derivative of this acid, the 2,4-dinitrophenylhydrazone, was synthesised[165]. The 2,4-dinitrophenylhydrazine reagent was prepared by dissolving powdered dinitrophenylhydrazine (0.5 g/0.0025 mol) in a mixture of concentrated hydrochloric acid (80 ml) and water (100 ml). The mixture was gently heated on a water bath. The solution was cooled, water was added and the solution was filtered.

A small amount of laevulinic acid (0.5 g/0.004 mol) was dissolved in distilled water (10 ml) and the 2,4-dinitrophenylhydrazine reagent (50 ml) prepared earlier was added. A yellow-orange compound separated, which was presumed to be the 2,4-dinitrophenylhydrazone of laevulinic acid.

After separation, this derivative was partly dissolved in boiling chloroform and filtered hot. The solution was left overnight at 1°C. The red-orange crystals obtained were filtered off. The melting point of these crystals was found to be 206-207°C (literature value 206°C[163] for the 2,4-dinitrophenylhydrazone of laevulinic acid). Thus, it can be concluded that the 2,4-dinitrophenylhydrazone of laevulinic acid was successfully prepared and that the identity of the compound labelled "laevulinic acid" was established.

The melting point of the laevulinic acid was found to be 31-34°C. According to the label on the bottle, the melting range should have been 33-35°C. Recrystallisation from a mixture of methanol, acetone and ethyl acetate gave white crystals whose melting point was 36-37°C. This compares well with the literature value of 37.2°C[164]. This purified laevulinic acid was used in the preparation of 4,4'-AB-4-CPA described in section 5.5.1. When the acid chloride of this 4,4'-AB-4-CPA was prepared, the infrared spectrum and melting point showed it to be identical to acid chloride II. At this point, it was concluded that the laevulinic acid supplied by Aldrich was not responsible for the failure in preparing acid chloride I.

5.10.3.5. Preparation of ammonium molybdate reagent for phosphorus test. Since the characterisations of laevulinic acid and 4,4'-AB-4-CPA had confirmed their identities, the possibility was next considered that the reaction between 4,4'-AB-4-CPA and phosphorus pentachloride had taken an unexpected course, perhaps resulting in the formation of some phosphorus-containing complex. In order to test this possibility, it was decided to analyse the product of this reaction for the presence of phosphorus. To carry out this analysis, an ammonium molybdate reagent was prepared. The reagent was obtained by dissolving commercial ammonium molybdate (4.5 g) in a mixture of concentrated ammonia solution (4 ml) and distilled water (6 ml). Ammonium nitrate (12 g) was added, and the solution was made up to 100 ml using distilled water.

5.10.3.6. Phosphorus test. A phosphorus test was first carried out on a sample known to contain phosphorus, i.e., triphenyl orthophosphate. The result was a bright yellow precipitate. Once this result was obtained, the

test for the presence of phosphorus in acid chloride II was performed. A few mg of acid chloride II (the same mole number as for triphenyl orthophosphate) were placed in a fusion tube and small lumps of sodium metal were added. The tube was heated gently at first and then vigorously until red hot. The red-hot tube was then dropped into distilled water (20 ml). The mixture was filtered. To 5 ml of the filtrate, concentrated nitric acid (15 ml) was added, and the mixture was boiled for a few minutes. It was allowed to cool and then a few ml of ammonium molybdate reagent were added. In the case of acid chloride II, only small traces of a yellow precipitate appeared. Thus it was concluded that the failure of acid chloride I to be prepared was not due to the formation of a phosphorus complex.

5.10.3.7. Attempts to prepare the acid chloride of itaconic acid. The chlorination of another available diacid was attempted in the hope that it would throw some light on the behaviour of 4,4'-AB-4-CPC. The diacid used was itaconic acid (methylenesuccinic acid), $CH_2=C(CO_2H)CH_2CO_2H$. Itaconic acid (2 g) and PCl_5(4 g) in benzene were left to react at room temperature for four hours but no reaction took place. Heating and allowing the reaction to proceed for 24 hours still produced no change.

5.10.4. Further attempts at solving the problem. 4,4'-AB-4-CPA was dissolved in boiling ethanol in order to eliminate possible small amounts of impurities[166] that might cause the reaction to follow a different path. The acid chloride derived from this acid had the infrared spectrum of acid chloride II. Another source of possible impurities could have been the solvent. Thus, redistilled benzene was used, but the distillation made no difference to the end product. Benzene was replaced by dichloromethane in the hope that the change in solvent would encourage the formation of acid chloride I, but acid chloride II was obtained. However, on repetition, acid chloride I was occasionally produced when dichloromethane was used as solvent and the 4,4'-AB-4-CPA used was that prepared in our laboratories. Also, acid chloride I was occasionally produced when the reaction was carried out in dichloromethane and a slight pressure was exerted. This could be achieved by carrying out the reaction in a closed reaction flask, since the evolution of hydrogen chloride gas increased the pressure within the flask. In general, but not always, acid chloride II

resulted if benzene was used as solvent in place of dichloromethane. On one occasion, the azo acid was washed with boiling diethyl ether, filtered and dried. It was reacted with PCl_5, the solvent being dichloromethane. The purification procedure was as described earlier. The product was acid chloride I. Yet the following day the result could not be repeated. The reaction was also carried out in a different laboratory from the one usually used. This new laboratory was in a different part of the Polytechnic. The result was acid chloride II.

No conclusions could be drawn from the above observations, since the results could not be reproduced.

As was stated earlier, different batches of phosphorus pentachloride produced acid chloride II. It was therefore decided to look for some other method for the preparation of the acid chloride of 4,4'-AB-4-CPA from the acid. The first chlorinating agent used was thionyl chloride. When thionyl chloride was used at room temperature on its own, i.e., in the absence of any other solvent, no reaction took place within two hours. The use of thionyl chloride in ether or benzene in the presence or absence of dimethylformamide still gave no reaction.

Several attempts were made to try to re-synthesise acid chloride I using dimethylformamide. Phosphorus pentachloride and dimethylformamide in benzene, but not in dichloromethane, gave acid chloride I. These experiments were carried out by Dr. A. C. Haynes. The mechanism of the reaction is said to be as follows[167,168]:

Dimethylformamide (1.5 ml) and phosphorus pentachloride (excess) were left in benzene for about ten minutes for the complex to form. Then 4,4'-AB-4-CPA (1 g) was added and the mixture was left for one hour.

The purification technique was identical to that employed for acid chlorides I and II obtained earlier. This procedure gave acid chloride I. The yield of acid chloride obtained with this method was 35%. The melting point of this batch of acid chloride I ranged from $85^{o}C$ to $95^{o}C$. Unfortunately, it is hard to define the melting point, since the compound melts and decomposes at the same time.

It was the acid chloride I from this particular batch that was used for the determination of chlorine content by the gravimetric method described in Section 5.10.3.3. As was stated earlier, the chlorine content corresponded to approximately two atoms per molecule, which is the expected result. Also, the decyl ester prepared from this particular batch of acid chloride gave a stable latex when used in the emulsion polymerisation of styrene in the absence of conventional surfactant.

The synthesis of acid chloride I following the dimethylformamide method was repeated a few times, but, as found with the methods used previously, this method also suddenly began yielding acid chloride II. It was found to be impossible to purify acid chloride I obtained by the PCl_5-dimethylformamide method.

In order to obtain adequately pure acid chloride I, therefore, it was proposed to use the Vilsmeier reagent to prepare the acid chloride from the acid. Hepburn and Hudson[169,170] report on the isolation of the Vilsmeier reagent, $[Me_2N{=}CHX]^{\oplus}X^{\ominus}$, where X is a halogen. These workers found that phosphorus pentachloride interacts with dimethylformamide to give the Vilsmeier reagent, and that the Vilsmeier reagent so prepared was a useful chlorinating agent.

The Vilsmeier reagent was prepared by the writer by the addition of phosphorus pentachloride (10 g) to an excess of dimethylformamide (28 g), allowing the temperature to rise to $100^{o}C$, followed by cooling in an ice bath at $0^{o}C$. The reaction mixture was filtered using a closed separating flask with nitrogen bubbling through, since the complex is a very hygroscopic substance. The white crystals were washed with dimethylformamide and ether, and then dried in a vacuum oven.

When the Vilsmeier reagent was reacted with 4,4'-AB-4-CPA in benzene, a layer of greenish substance was obtained, which was discarded, since the acid chloride in both forms is soluble in benzene. The benzene was evaporated and a yellow oil recovered. Unfortunately, this oil was insoluble in ether, whereas both acid chlorides are soluble in ether. Thus, the attempt at synthesising 4,4'-AB-4-CPC using the Vilsmeier reagent failed.

Procedures for the synthesis of esters from the parent acid and the appropriate alcohol at room temperature can be found in the literature[171-172]. The method employed by Reed[173] and by Bourne et al[174] was investigated in an attempt to obtain the decyl ester of 4,4'-AB-4-CPA without using the acid chloride. The method involves the use of trifluoroacetic anhydride. 4,4'-AB-4-CPA (5.4 g/0.02 mol) was dissolved in excess trifluoroacetic anhydride (8.4 g/0.04 mol) used as solvent as well as reagent. To this mixture, decanol (6.3 g/0.04 mol) was added and left to react for three hours. The mechanism for the formation of esters by this reaction is believed to be as follows:

$$RCOOH + (CF_3CO)_2O \rightleftharpoons RC(O)\text{-}O\text{-}C(O)CF_3 + CF_3COOH$$

$$RC(O)\text{-}O\text{-}C(O)CF_3 \rightleftharpoons RCO^{\oplus} + CF_3COO^{\ominus}$$

$$RCO^{\oplus} + R'OH \longrightarrow RCOOR' + H^{\oplus}$$

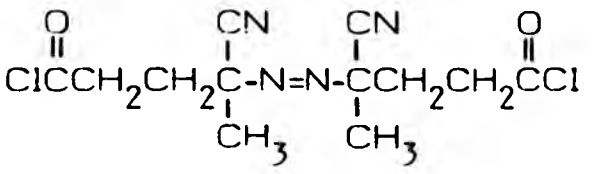
$$H^{\oplus} + CF_3COO^{\ominus} \longrightarrow CF_3COOH$$

The infrared spectrum of the substance obtained showed the presence of a carbonyl peak, but it failed to reveal the presence of any nitrile groups. The results of elemental analysis that nitrogen was not present in this product. It was therefore concluded that this preparative route had failed to produce the desired compound, and this synthetic procedure was consequently abandoned.

5.11. A possible explanation of the problem. The conclusion has been drawn that 4,4'-AB-4-CPA reacts with PCl_5 to give two different forms of 4,4'-AB-4-CPC. Both forms of the acid chloride react with two mol of

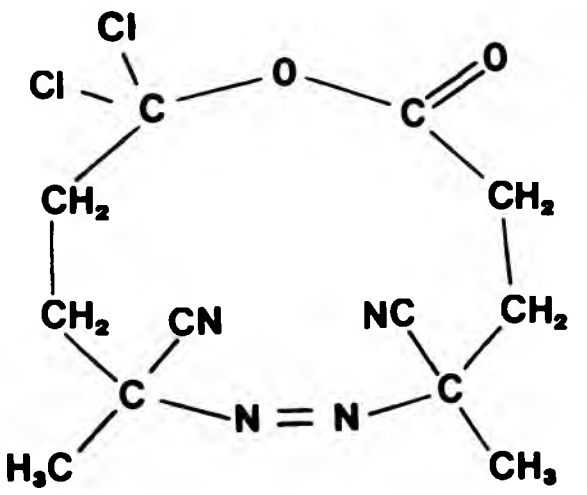
alcohol to give esters. Thus, it appears that 4,4'-AB-4-CPC may exist in two structurally different isomeric forms.

One form in which 4,4'-AB-4-CPC may exist is the straight-chain structure, i.e.,



(a)

The other form is envisaged as being a cyclic structure. One possibility is



(b)

An eleven-atom-member ring is not a particularly stable configuration, and it is expected that the open chain would be favoured. Unfortunately, neither of the two structures given above is consistent with the infrared spectrum of acid chloride I.

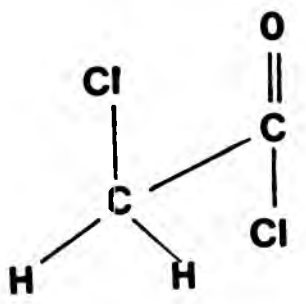
The infrared spectrum of acid chloride I (Fig. 5.1) has two carbonyl peaks and a wide OH-like band around 3500 cm^{-1}. The obvious conclusion to draw from such evidence is that incompletely reacted acid is present in the acid chloride. This would be consistent with the presence of a second carbonyl peak and of the OH-like band in the infrared spectrum, and indeed, when acid chloride II is allowed to hydrolyse partially, the infrared spectrum of the resulting product can be identical to that of acid chloride I if sufficient hydrolysis occurs. However, this hydrolysed mixture is partially insoluble in benzene and in dichloromethane. The portion that dissolves in either benzene or dichloromethane can be recrystallised to yield acid chloride II. The portion that is insoluble in either solvent is, according to infrared analysis, 4,4'-AB-4-CPA. Now, since both acid

chloride I and acid chloride II are completely soluble in benzene and in dichloromethane, whereas a sample of partially hydrolysed acid chloride II is partly insoluble in both solvents, with the free acid being insoluble, it follows that, in spite of the identity of their infrared spectra, acid chloride I cannot be identified as partially hydrolysed acid chloride II.

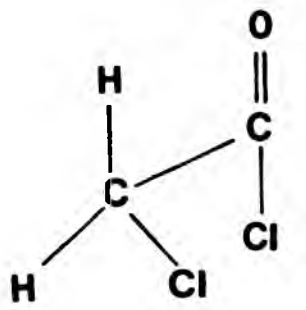
^{13}C NMR would pick up a strong signal due to free acid. A spectrum was run specifically to look for acid groups in acid chloride I; none was observed. Whatever groups are responsible for the second carbonyl and OH-like band in the infrared spectrum of acid chloride I, the evidence does not support the idea that these bands are due to the presence of acid in the acid chloride.

Both acid chlorides react with two mol of alcohol to give -- presumably -- the corresponding esters. Fig. 5.2 shows the infrared spectrum of the decyl ester obtained using acid chloride I. As can be seen from the spectrum, there is no presence of OH and neither is there a second carbonyl peak. The infrared spectra of the decyl esters obtained using acid chlorides I and II are identical, as are the ^{13}C NMR spectra.

According to the literature, it seems that the spectra of mono- or disubstututed alpha-halogeno acid halides can show two carbonyl absorptions. Doubling of the bands occurs in the vapour phase, as well as in the liquid phase or in solution. Avram and Mateescu[175] claim that the increased number of bands is due to the conformational isomers (c) and (d) below:



(c)

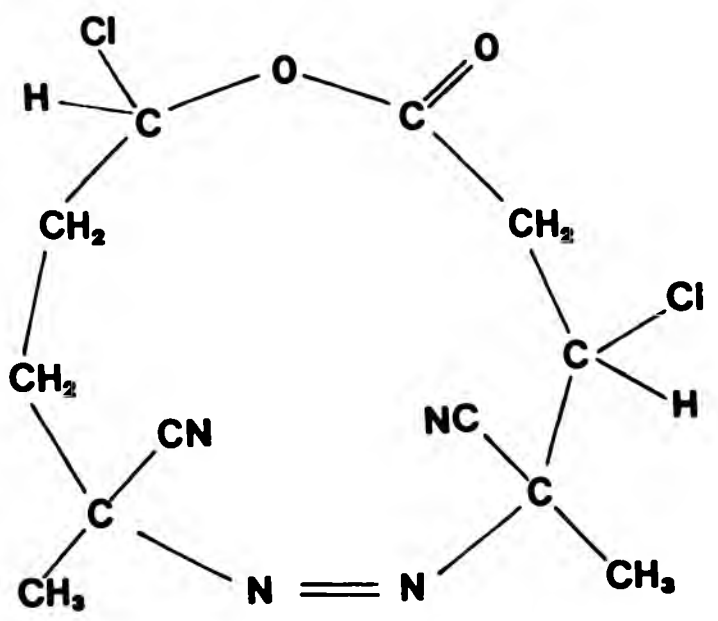


(d)

Their proposal seems to predict that in the solid state the more stable isomer should have the more polar conformation (c), with chlorine and oxygen atoms cis to each other. This conformation, according to the authors, should give rise to a band at higher frequency than conformation (d).

Under these conditions, spectra of chloroacetyl and dichloroacetyl chloride show the two bands corresponding to conformations (c) and (d). Trichloroacetyl chloride has a single band, as does acetyl chloride. The abnormal behaviour of alpha-halogenated carbonyl compounds has been attributed to the field effect of the chlorine atom which in conformation (c) is cis to the oxygen atom and in conformation (d) is rotated by 120^{o}. The increase in the carbonyl frequency is due primarily to the -I effect of the chlorine atom attached to the C=O group.

Another cyclic structure which acid chloride I could have is (e):



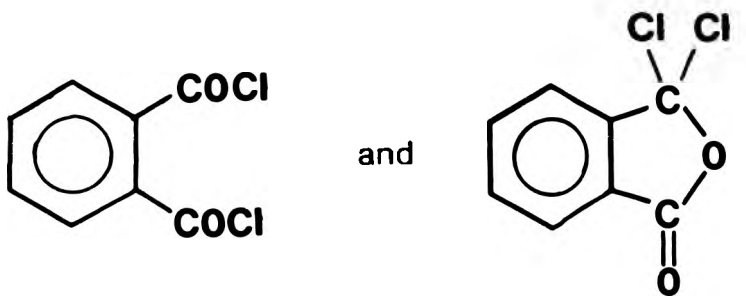
(e)

Since the ring is large enough to permit some rotation of the C-C bonds, it would apparently be possible for the alpha-chlorine atom to stand in either of two distinct positions with respect to the carbonyl oxygen: either cis or staggered. By analogy with the proposals of Avram and Mateescu, therefore, structure (e) might also exhibit two carbonyl peaks in the infrared. The OH-like band, however, is difficult to account for with structure (e). The isomers of alpha-substituted acid chlorides also have different solubilities.

5.12. Structural isomers of diacid chlorides.

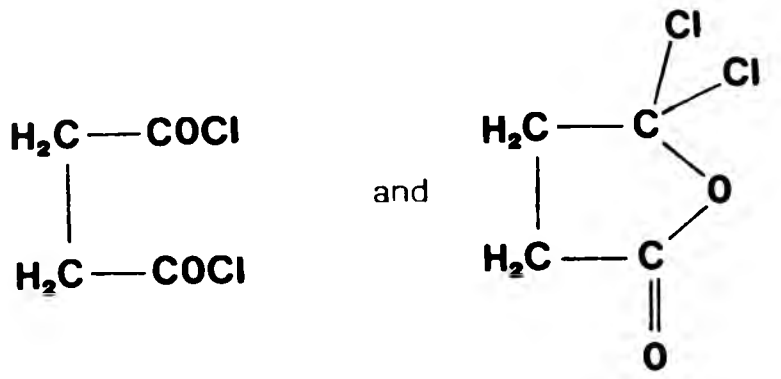
5.12.1. Introduction. Certain diacid chlorides can exist in two different modifications. These two tautomers, i.e, isomers which differ only in the relative position of an atom, have different physical properties as well as different infrared spectra. One form of the diacid chloride has one carbonyl peak in the infrared, whilst the other structure shows two carbonyl peaks. The reader will be aware that these are some of the main characteristics shown by acid chloride I and acid chloride II, respectively. Below is a review of the published literature on some structural isomers of diacid chlorides.

5.12.2. Review of some possibly relevant work reported in the literature. According to Wheland[176], some acid chlorides of dibasic acids show ring-chain tautomerism. Ring-chain tautomerism can be regarded as a special kind of prototropy or aniotropy, since the tautomeric structures always differ in the position either of a proton or of an anionic atom or group. Phthaloyl chloride, for example, reacts as if it has both of the structures below:

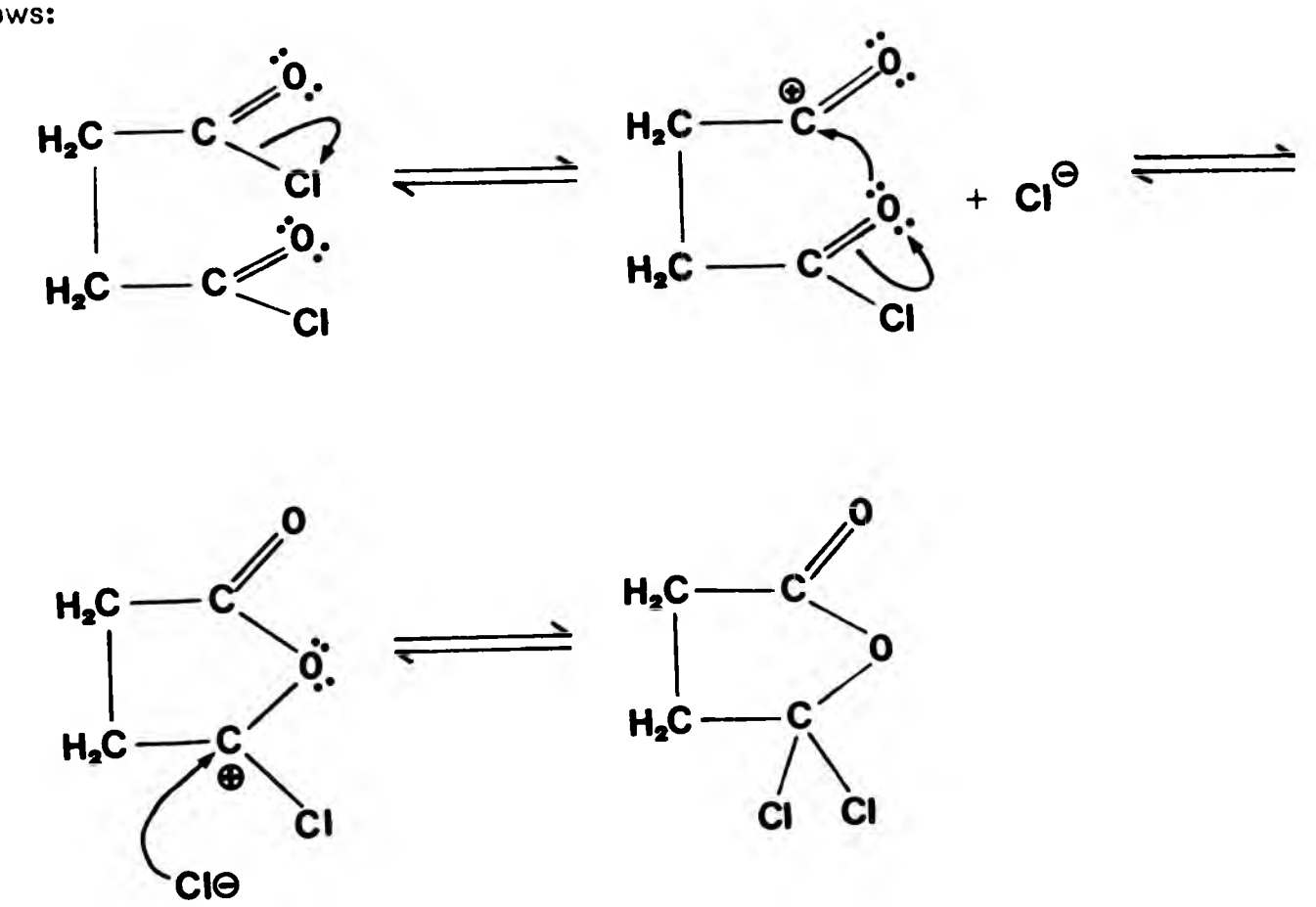


That the two tautomers actually exist has been proven by the isolation of each.

Succinyl chloride is similarly tautomeric, since its reactions are consistent with its being a mixture of the following structures:



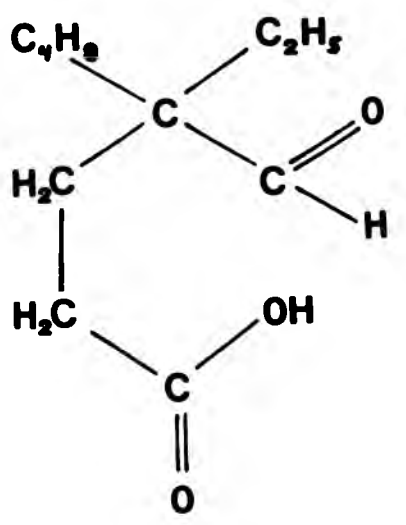
Cason and Smith[177] maintain that rearrangement occurs on forming an acid chloride from a half-ester with impure thionyl chloride, but they were unable to obtain rearrangement by the use of technical thionyl chloride, or by the addition of 10 mol % sulphonyl chloride to the thionyl chloride. They concluded that it is most probable that the thionyl chloride giving the rearrangement contained a metallic salt, for a preparation to which 4 mol % of ferric chloride was added gave extensive rearrangement. It is postulated that the rearrangement proceeds as follows:

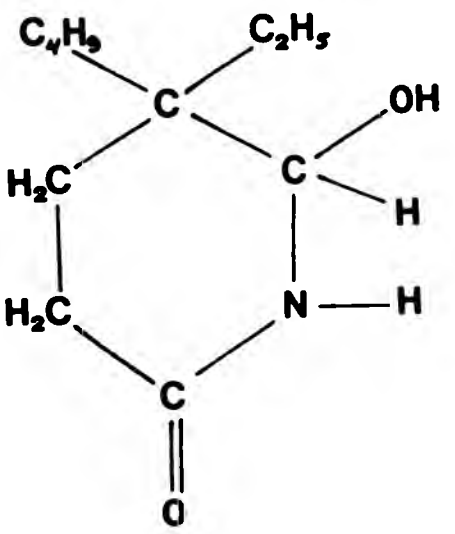


The above is the mechanism of catalysis by $FeCl_3$ proposed by Cason and Smith[177]. These workers suggest that their data indicate that diacid chlorides such as succinyl dichloride have the normal open-chain structure as indicated by infrared analysis, and that the cyclic reaction products are formed from the open-chain structure by way of cyclic intermediates. Numerous physical measurements have indicated that succinyl dichloride exists predominantly in the open-chain form, and that the cyclic form is a minor component. These measurements are said to have included refractivity, dipole moment, and molecular volume, among others.

Cason and Reist[178] found that the open-chain compound gives an infrared spectrum showing two carbonyl peaks. In their investigations, they found that the infrared spectra of laevulinyl chloride and of -keto acid chlorides show that these compounds exist at room temperature, entirely or predominantly, as cyclic structures. In each case, there is only one absorption band corresponding to the carbonyl group. Thus, although a diacid chloride and an ester acid chloride are stable in an open-chain form, these authors claim that "the presence of an alkyl substituent on the second carbonyl group causes ready conversion to the cyclic structures".

The ester of γ-ethyl-γ-formylcaprylic acid appears to be mainly open-chain, whereas the amide appears to have mainly a cyclic structure[177]:



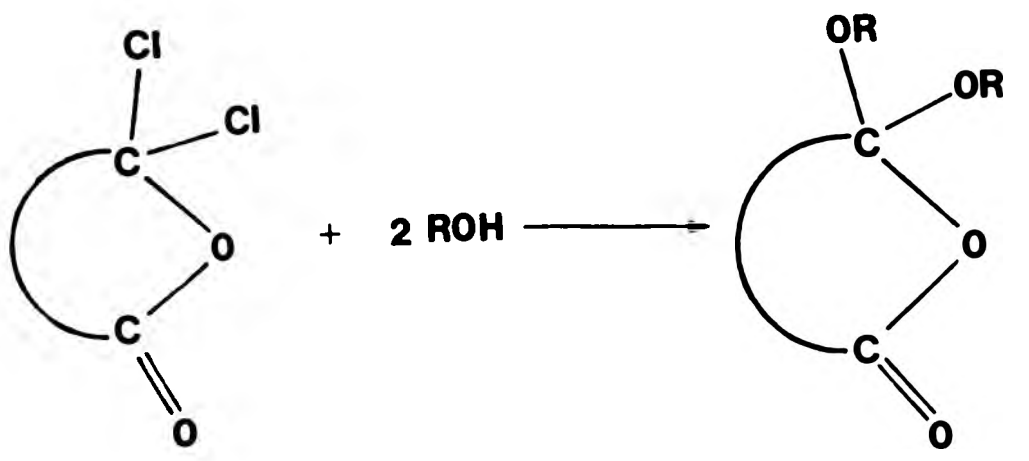


γ-ethyl-γ-formylcaprylyl chloride[178] is especially interesting in that it exists partly in the open-chain form and partly in the cyclic form.

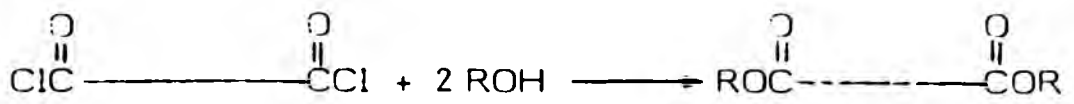
5.12.3. Relevance to the present work. 4,4'-AB-4-CPC is a diacid chloride, some batches of which give an infrared spectrum with one carbonyl peak and other batches of which give an infrared spectrum with two carbonyl peaks. These two types of compound have been designated as "acid chloride I" and "acid chloride II". In view of this, the above structural considerations could not be rejected without investigation. Furthermore, the esters of acid chloride I behaved as stabilisers for emulsion polymerisation in the absence of conventional surfactant, whilst the amides did not. However, there is no evidence that 4,4'-AB-4-CPC forms structural isomers of this particular type. Ferric chloride was added in order to encourage rearrangement, to no avail, and the esters derived from acid chloride I were placed in concentrated hydrochloric acid, where they should have reverted to the open-chain form if they were cyclic structures; but no apparent change took place.

In the two cases for which ring-chain tautomerism seems to have been established, ring formation is possible because the ring is five-membered. The end groups are then sufficiently close for them to react with one another. In the case of the proposed cyclic structure for 4,4'-AB-4-CPC, the ring would have to comprise eleven atoms. The end groups are thus probably too far apart for easy interaction.

Also, the infrared spectra of both putative esters show that they are indeed esters, and it is difficult to envisage an esterification reaction of the cyclic acid chloride giving esters. One possible reaction is as follows:



But the product shown does not have the structure of a conventional ester. The open-chain structure would yield normal esters.



5.13. Conclusions. 4,4'-AB-4-CPA reacts with phosphorus pentachloride to give two different types of acid chloride. The two types have been labelled 'acid chloride I' and 'acid chloride II'. Acid chloride I is more pungent than acid chloride II. Both acid chlorides react with two mol of an alcohol, e.g., decanol, to give two different putative esters; these esters have been called 'ester A' and 'ester B', where ester A is derived from acid chloride I and ester B is derived from acid chloride II. Whatever was the cause of the differences in the acid chlorides, these differences appear to be maintained in the corresponding esters; i.e., the conformational, structural or other isomerism that may be responsible for the differences in the acid chloride is transmitted to the esters. The decyl ester A, for instance, has the typical smell of an ester, is a yellowish wax and is, surprisingly, somewhat soluble in water. The decyl ester B, in contrast, is an odourless white wax and, furthermore, its solubility in water, hot or cold, is practically nil. It appears that, because of the partial solubility of the decyl ester A in water, this compound produces a polystyrene latex when used in the emulsion polymerisation of styrene in the absence of conventional surfactant. The decyl ester B does not behave in this way. The latices produced by the straight-chain esters derived from acid chloride I in the absence of conventional surfactant are all stable and monodisperse with solid contents which are unusually high for a surfactant-free emulsion polymerisation reaction. Given the above properties shown by type A esters, it was only natural that a considerable effort was put into preparing acid chloride I after the sudden failure to prepare it by the hitherto satisfactory route. Unfortunately, no conclusions can be drawn from the results obtained in this part of the investigation, since they are not reproducible. Why some particular procedure yielded acid chloride I sometimes and just as often gave acid chloride II remains a frustrating mystery.

Even if the possibilities of conformational or structural isomerism cannot be completely discarded, they remain only a suggestion, a speculative attempt at solving the problem of the existence of two different acid chlorides of 4,4'-AB-4-CPA.

CHAPTER SIX

MORE DETAILED INVESTIGATIONS OF ESTERS OF FATTY-ALCOHOL ETHOXYLATES AS INITIATOR/STABILISERS

6.1. Introduction. At this point, the attempts at preparing 4,4'-azobis-4-cyanopentanoyl chloride I were abandoned. Thus the work carried out from this point was based upon the reaction products obtained from 4,4'-azobis-4-cyanopentanoyl chloride II.

It has already been reported in Chapter Five that the straight-chain esters derived from acid chloride II do not yield latices when used as initiator/stabilisers in the emulsion polymerisation of styrene in the absence of conventional surfactant. Therefore other esters were prepared from acid chloride II in an attempt to obtain other compounds that would act as both polymerisation initiators and stabilisers for polymer latices. The first such ester investigated was that obtained using 11-hydroxyundecanoic acid. The potassium salt of this acid failed to give a latex when used as initiator/stabiliser for the emulsion polymerisation of styrene. During the earlier stages of the reaction (approximately 15 minutes), a milky latex-like product was observed. As time went on, this changed into a greyish solution. pH measurements showed that a reduction from 11 to 8 had occurred. The high pH was the result of excess KOH in the solution; it seemed that the ester might have been hydrolysed under the strongly alkaline conditions of the reaction medium. Yet the same reaction using the corresponding ester prepared from acid chloride I had yielded stable and monodisperse latices. The reaction was again repeated using the corresponding ester obtained from acid chloride II, but in this case the initial pH was approximately 8 instead of 11. At the end of two and a half hours at $70^{o}C$, a considerable amount of styrene remained unreacted.

Of the various 4,4'-AB-4-CPC derivatives described in Chapter Five, the only group of successful latex-yielding compounds to be prepared using acid chloride II was the esters of various fatty-alcohol ethoxylates supplied by ABM Chemicals as their "Texofor A" range. Acid chlorides are assumed to react with the terminal hydroxy group of these ethoxylates to

yield esters. Some of the compounds obtained from acid chloride II behave as initiator/stabilisers for the emulsion polymerisation of styrene. The synthetic procedure was identical to that given in Chapter Five for the synthesis of these esters from acid chloride I. A series of esters of various fatty-alcohol ethoxylates has been prepared. The esters varied in respect of the number, n, of ethylene oxide units per molecule of hydrophobe base in the ethoxylate. n varied from 2 to 60. The esters of $FA(EO)_2$, $FA(EO)_6$ and $FA(EO)_{10}$ were found to be insoluble in water and did not produce latices when used as initiator/stabilisers for the emulsion polymerisation of styrene. The esters of $FA(EO)_{14}H$, $FA(EO)_{24}H$, $FA(EO)_{45}H$ and $FA(EO)_{60}H$ did yield stable latices when similarly used.

6.2. Preliminary kinetic studies. A preliminary kinetic study was carried out in order to establish the relative efficiencies of these compounds as initiator/stabilisers.

6.2.1. Procedure. A conventional multi-neck reaction vessel was used fitted with a stirrer, a condenser and a nitrogen inlet. Since the system appeared to be macroscopically homogeneous, the conversion of monomer to polymer was followed by withdrawing samples from the reaction flask at appropriate intervals. To each sample, two drops of a solution of tert-butylcatechol solution (approximately 0.1% in toluene) were added and the sample was evaporated to dryness to obtain the solids content. Conversion was calculated from the solids content by the following equation:

$$C = SF_1 - F_2$$

$$\text{where } F_1 = \frac{I + M + W}{M}$$

$$\text{and } F_2 = \frac{100\,I}{M}$$

and where S is the % solids content, C is the % conversion, I is the weight of initiator, M is the weight of monomer and W is the weight of water, in an arbitrary mass of reaction system.

6.2.2. Recipes used in the preliminary studies. The first recipe used was as follows:

styrene	40 ml
water	100 ml
ester	1.1×10^{-3} mol

These results are given in Fig. 6.1.

The formulation above was such that the molecular concentration of the initiator was kept constant throughout the series. The final pH of the reaction system was approximately 7.

A second series of reactions was carried out using the following recipe in which the weight of the ester was kept constant:

styrene	40 ml
water	100 ml
ester	5.0 g

The results obtained are given in Fig. 6.2. In both series of reactions the temperature of the reaction mixture was kept at 50^{o}C.

6.2.3. Discussion of preliminary results. Examination of the conversion-time curves shown in Figs. 6.1 and 6.2 reveals that in some cases the progress of the reaction is similar to that observed in conventional emulsion polymerisation reactions. In other cases, however, the polymerisation appears to follow a rather different course. Specifically, the conversion-time curves for the reactions initiated and stabilised by $FA(EO)_{45}Es$ and $FA(EO)_{60}Es$ resemble those for conventional emulsion polymerisation, except that the linear portion, i.e., the constant-rate period, extends in some cases to 80% conversion before the rate begins to tail off, whereas those for reactions initiated and stabilised by $FA(EO)_{24}Es$ and $FA(EO)_{30}Es$ do not. The conversion-time curves for reactions initiated by the latter compounds can be best described as a series of straight lines of decreasing slope. The reason why the writer prefers to regard these conversion-time curves as consisting of series of straight lines of decreasing slope, rather than as smooth curves, will be

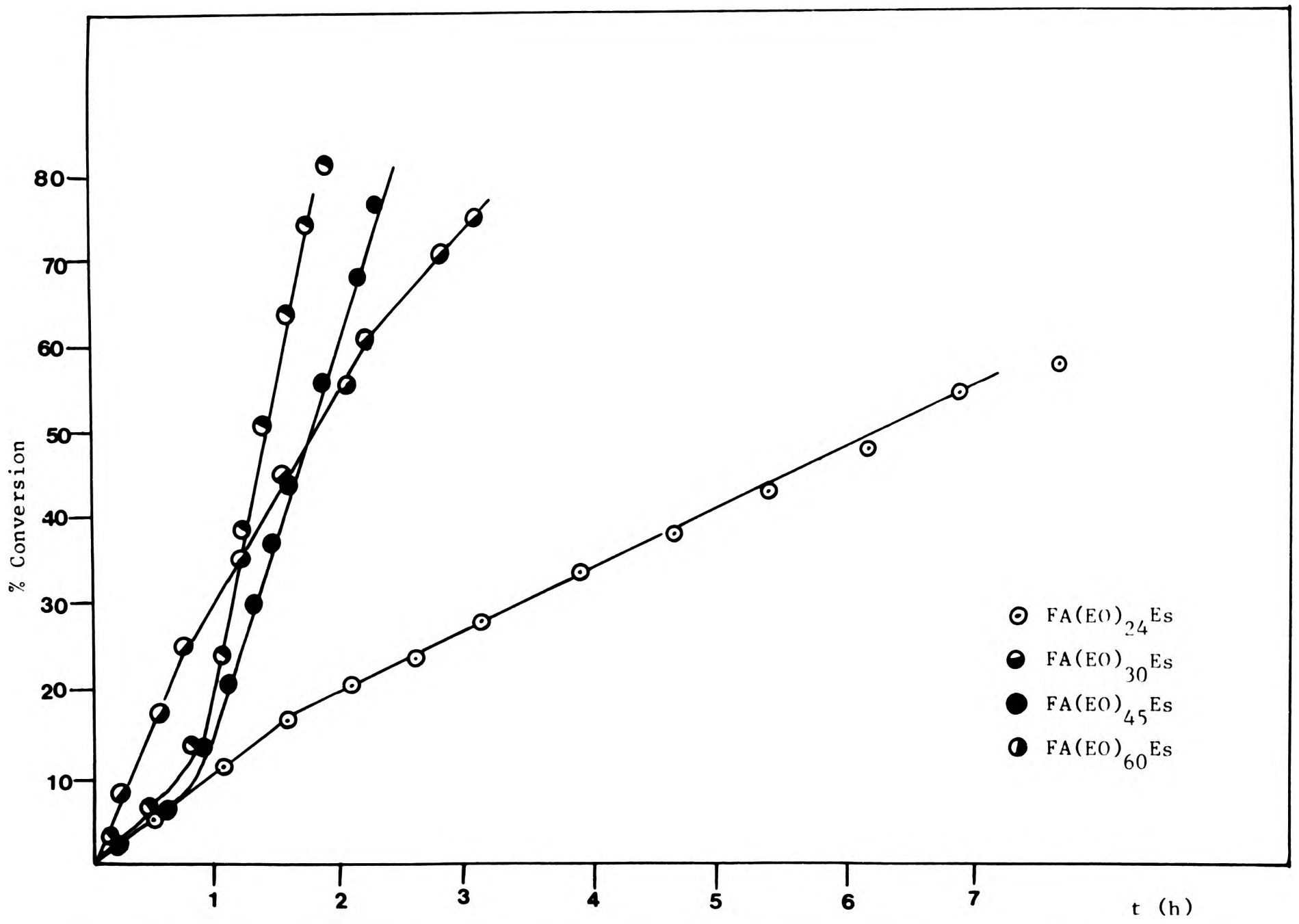


Fig. 6.1: Conversion-time curves for emulsion polymerisation of styrene at 50°C using various fatty-alcohol ethoxylate esters as initiator/stabilisers: constant molar amount of ester

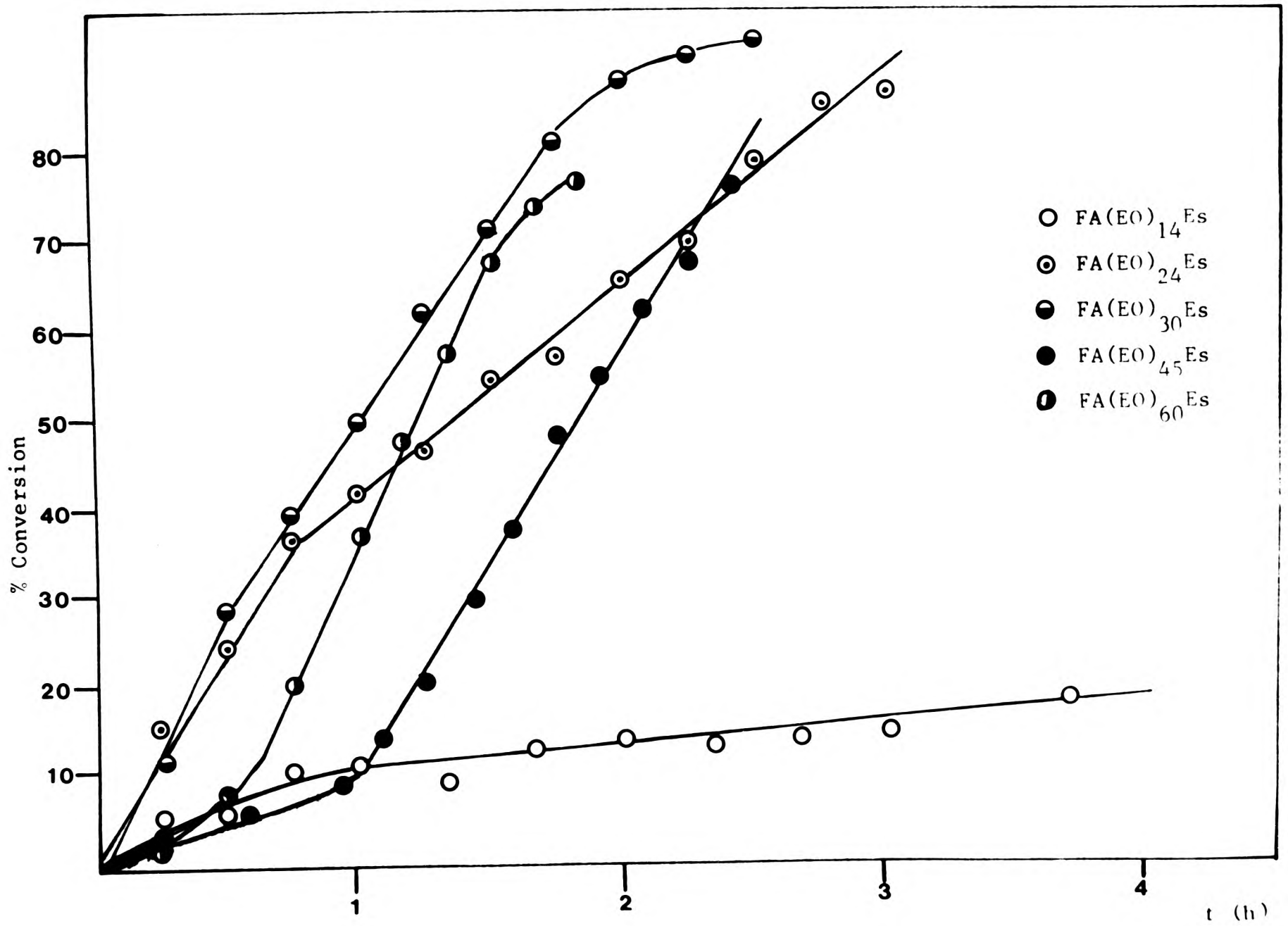


Fig. 6.2: Conversion-time curves for emulsion polymerisation of styrene at 50°C using various fatty-alcohol ethoxylate esters as initiator/stabilisers: constant weight of ester

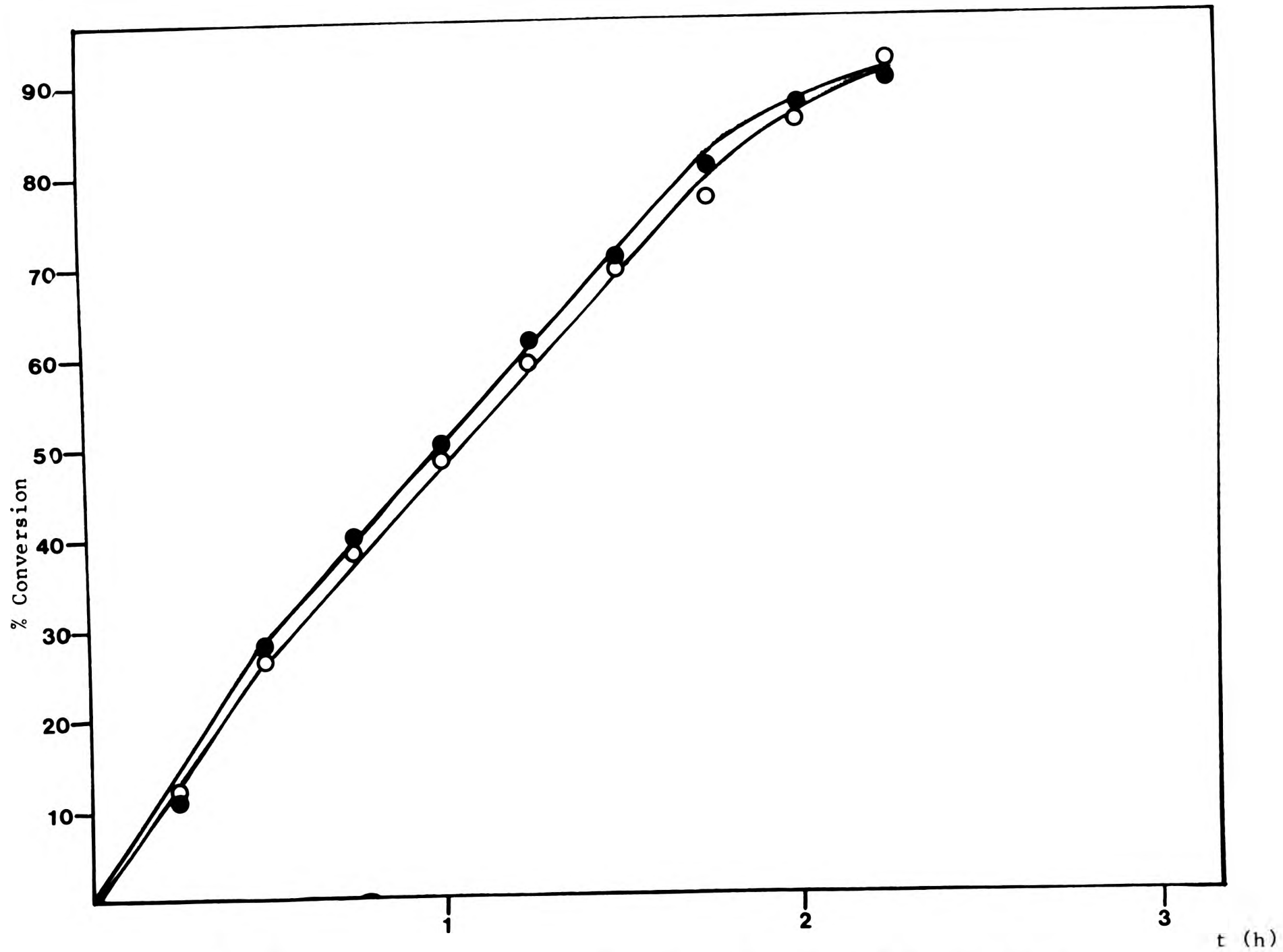


Fig. 6.3: Results of experiments to check reproducibility of styrene emulsion polymerisations using $FA(EO)_{30}Es$ as initiator/stabiliser at 50°C.

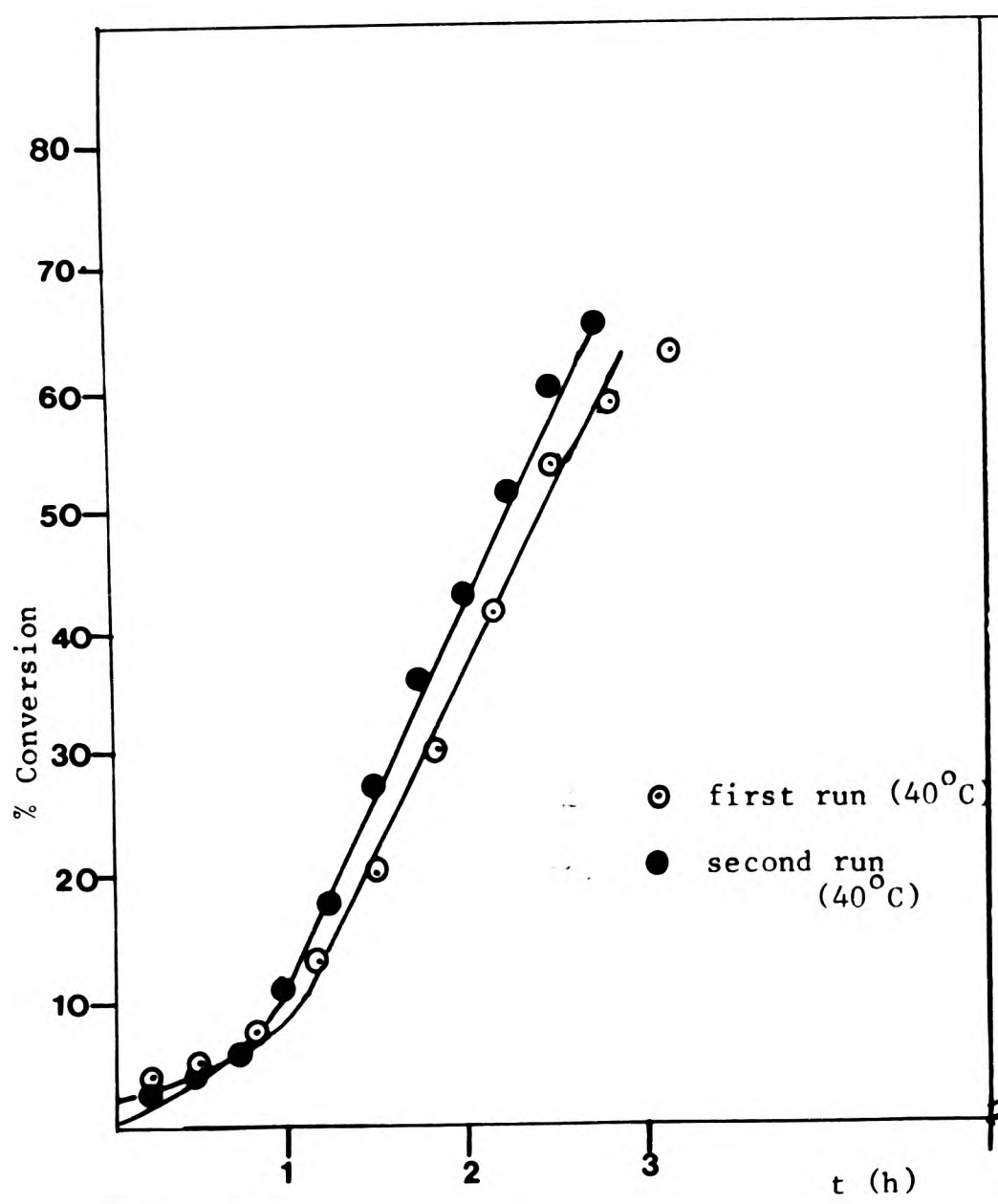


Fig. 6.4a: Results of experiments to check reproducibility of styrene emulsion polymerisations using $FA(EO)_{60}Es$ as initiator/stabiliser.

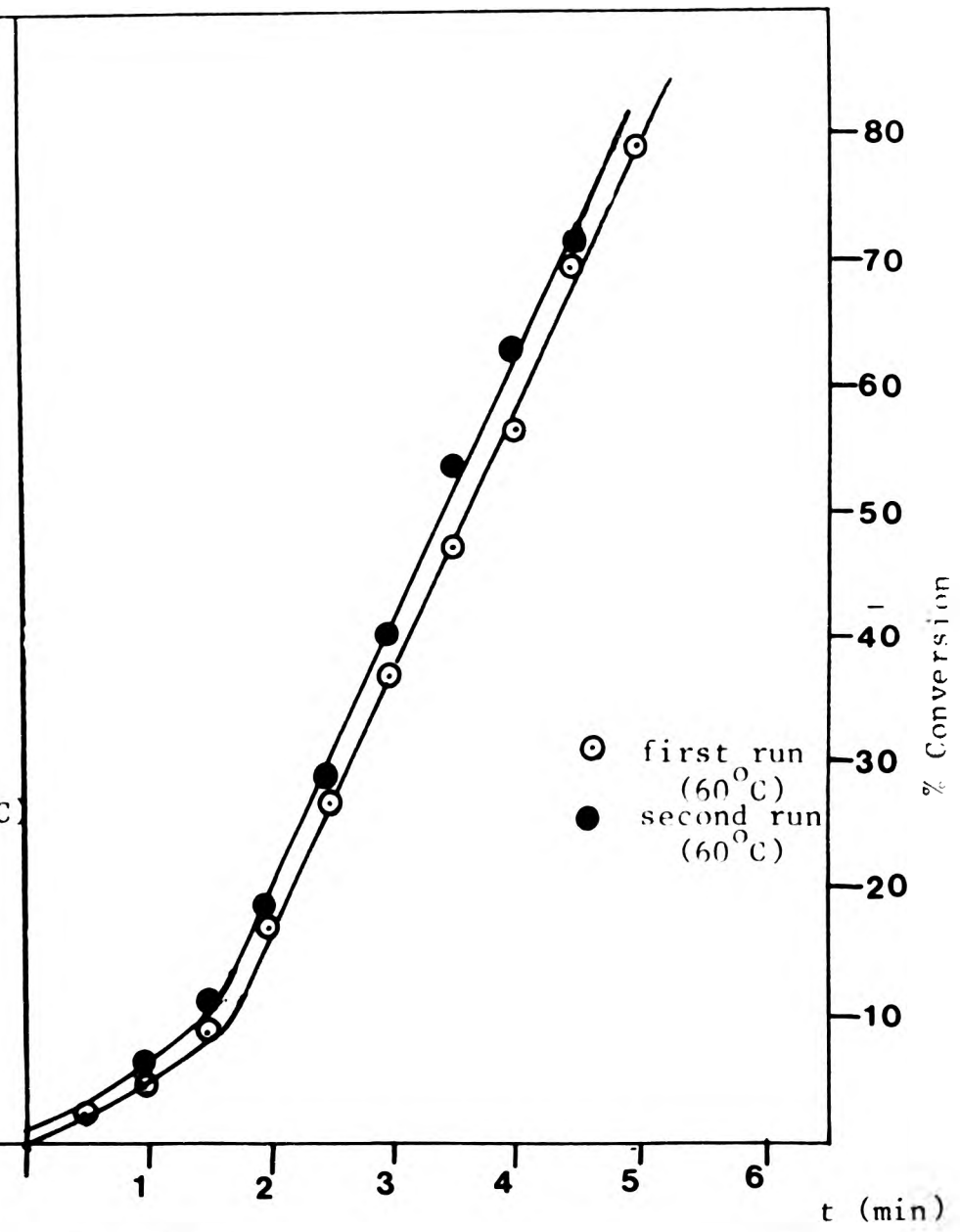


Fig. 6.4b: Results of experiments to check reproducibility of styrene emulsion polymerisations using $FA(EO)_{60}Es$ as initiator/stabiliser.

made apparent in Chapter Seven.

The shapes of these curves suggest that the polymerisation reaction may proceed in the case of reactions initiated by $FA(EO)_{24}Es$ and $FA(EO)_{30}Es$ by a different pathway than in the case of a conventional emulsion polymerisation. Specifically, two important points of difference can be observed:

(1) Apparently there is no nucleation period, and

(2) The rate of polymerisation decreases as the reaction proceeds instead of increasing.

Hence, it appeared to be worthwhile to investigate these reactions in further detail, and to try to determine the conditions under which the unusual conversion-time curves are observed. To do this, a number of experiments were carried out in order to study the effects of certain variables. However, before proceeding any further, the reproducibility of styrene emulsion polymerisations using $FA(EO)_{30}Es$ and $FA(EO)_{60}Es$ as initiator/stabiliser was examined. The results of these experiments are shown in Figs. 6.3 and 6.4, respectively. The reproducibility was found to be satisfactory; it was therefore possible to proceed with confidence to the study of these variables.

6.3. Effect upon the rate of emulsion polymerisation of styrene of (1) the concentration of ester, (2) the temperature and (3) the total volume of water. The first variable to be studied was the effect upon the rate of emulsion polymerisation when the concentration of initiator/stabiliser was varied. The temperature of the reaction was maintained at $50^{o}C$ and the volume ratio of styrene to water was 40:100. The esters studied were those of $FA(EO)_{24}H$, $FA(EO)_{30}H$, $FA(EO)_{45}H$ and $FA(EO)_{60}H$. The study of $FA(EO)_{14}Es$ was abandoned because of the low polymerisation rates obtained even at high initiator initiator/stabiliser concentrations (see Fig. 6.2).

In conventional emulsion polymerisation, an increase in the concentration of initiator results in an increase in the rate of polymerisation. One of the reasons for this experiment was to determine the order of reaction with respect to the amount of initiator and stabiliser. Moreover, since

the conversion-time curves for emulsion polymerisation reactions initiated by $FA(FO)_{45}Fs$ and $FA(FO)_{60}Fs$ are broadly similar to those for conventional emulsion polymerisation reactions, the object of these experiments was to determine whether, on increasing the concentration of the initiator, the rate of polymerisation increased also. In the case of reactions initiated by $FA(FO)_{24}Fs$ and $FA(FO)_{30}Fs$, the object of the experiment was to observe what happens when the concentration of the ester was increased; i.e., any changes in the shape of the curves, the dependence of the rate of polymerisation upon the concentration of initiator, etc.

The results of the effect upon the rate of polymerisation of styrene of the ester concentration are given in Figs. 6.5 - 6.8.

The second variable to be studied was the effect of temperature upon the rate of emulsion polymerisation of styrene. The reasons for carrying out these experiments were as above, i.e., to compare these results with those of conventional emulsion polymerisation reactions. The concentration of the ester in these experiments was maintained at 1.1×10^{-3} mol per 40 ml of styrene. The volume ratio of styrene to water was 40:100. The results of these experiments are given in Figs. 6.9 - 6.12.

A particularly interesting observation from these experiments was that the shapes of the conversion-time curves for the emulsion polymerisation of styrene using $FA(FO)_{24}Fs$ and $FA(FO)_{30}Fs$ as initiator/stabilisers became similar to those for conventional emulsion polymerisation reactions if the polymerisation temperature was reduced. This is illustrated by the results obtained using $FA(FO)_{24}Fs$ at $35^{o}C$ and $FA(FO)_{30}Fs$ at $45^{o}C$.

Since temperature seemed to affect the shape of the conversion-time curves when $FA(FO)_{24}Fs$ and $FA(FO)_{30}Fs$ were used as initiator/stabilisers, additional experiments were carried out in order to investigate the matter further. The effect upon the rate of polymerisation of styrene of the concentration of $FA(FO)_{24}Fs$ and $FA(FO)_{30}Fs$ was studied as before, but the temperature was reduced to $45^{o}C$. Figs. 6.13 and 6.14 give the results obtained.

By this stage, the results seemed to indicate that the partition of the ester between water and styrene might be an important factor in determining the shape of the conversion-time curve. Direct measurements of the partitioning of the esters in styrene and water could not be accomplished, since it was not possible to separate the styrene and the water layers clearly, presumably because the ester functioned as an emulsifier for styrene and water.

However, it was thought it might be of interest to investigate the effects of increasing the total volume of water in the reaction system whilst maintaining the amount of styrene and initiator constant. In particular, it was thought that the shape of the conversion-time curve might be changed. Also, it was hoped to obtain information concerning the effect upon the rate of emulsion polymerisation of styrene of varying the total volume of water in the reaction system. The amount of ester used was 1.1×10^{-3} mol per 40 ml of styrene, the temperature of the polymerisation was $45^{o}C$, and the volume ratios of styrene to water were as follows: (a) 40:72, (b) 40:100, (c) 40:145 and (d) 40:181. The results obtained are shown in Figs. 6.15 - 6.18.

6.4. Effect upon the rate of emulsion polymerisation of styrene of varying the temperature when $FA(EO)_{24}Es$ was used as initiator/stabiliser and when the total volume of water was increased. The next step was to study the effect of varying the temperature upon the emulsion polymerisation of styrene when $FA(EO)_{24}Es$ was used as initiator/stabiliser and when the total volume of water was increased, in order to investigate the effect of temperature upon the shape of the conversion-time curve when the water content of the reaction system was increased. The amount of ester was 1.1×10^{-3} mol per 40 ml of styrene. The volume ratio of styrene to water was 40:145. Fig, 6.19 shows the results obtained.

6.5. Reproducibility studies. During the preliminary kinetic work, the reproducibility of the conversion-time curves was investigated. These investigations included reaction systems which gave conventional conversion-time curves like the curves obtained when $FA(EO)_{60}Es$ was used as initiator/stabiliser at various polymerisation temperatures, and

also reaction systems which gave unusual conversion-time curves like the curves obtained when $FA(EO)_{30}Es$ was used as initiator/stabiliser at 50°C. The results of these experiments are given in Figs. 6.3 and 6.4. However, investigation of the effect of temperature upon the rate of polymerisation and the shape of the conversion-time curves obtained when $FA(EO)_{24}Es$ and $FA(EO)_{30}Es$ were used as initiator/stabilisers revealed further unexpected results when the polymerisation temperature was higher than 50°C. It was therefore necessary to investigate the reproducibility of these observations. Fig. 6.20 gives the results obtained. The results show that the shapes of the curves can be reproduced satisfactorily. Unfortunately this is not the case for the reproducibility of the rates of polymerisation.

6.6. Surfactant properties of $FA(EO)_{30}H$ and $FA(EO)_{60}H$ and of their 4,4'-azobis-4-cyanopentanoic acid esters.

6.6.1. Introduction. Because of the unexpected nature of some of the results obtained for the emulsion polymerisation of styrene using the fatty-alcohol ethoxylates as initiator/stabilisers, it was thought desirable to investigate some of the surfactant properties, i.e., the critical micelle concentration, in order to obtain evidence of micelle formation by both $FA(EO)_{30}H$ and $FA(EO)_{60}H$ and the esters derived form them; i.e., $FA(EO)_{30}Es$ and $FA(EO)_{60}Es$ were studied. The results obtained from these experiments are shown in Figs. 6.21 and 6.22.

6.6.2. Procedure. In these experiments deaerated doubly-distilled water was used. The temperature of the experiments was 25°C ± 0.5°C. $FA(EO)_{30}H$ and $FA(EO)_{60}H$ are known to have well-defined critical micelle concentrations (c.m.c.). The procedure followed was that described in the literature[179]. An initial solution was made by dissolving 0.089 g of $FA(EO)_{30}H$ in 100 ml of distilled water. In the case of $FA(EO)_{60}H$, 0.091 g was dissolved in 100 ml of distilled water. The surface tension of these original solutions was measured and also that of subsequent dilutions. The surface tension of distilled water was also measured. The surface tension of deaerated distilled water at 25°C was found to be 71.5 dyne/cm. The surface tension at different dilutions was plotted against the log of the concentration of the fatty-alcohol

ethoxylates. The procedure followed was that given in Chapter Five, section 5.7.5.5. The procedure followed in the case of the esters was identical to that used for the fatty alcohol ethoxylates.

6.7. Solubility of fatty-alcohol ethoxylate esters in water at different temperatures. Observations on the solubility of the fatty-alcohol ethoxylate esters in water at different temperatures are given in Table 6.1. From these observations, the approximate cloud points have been estimated; these are also given in Table 6.1. The reason for undertaking these experiments was to find the temperature at which the esters became insoluble in water. All the polymerisations in this chapter have been carried out below this temperature. The half-lives of the esters at different temperatures are given in Table 6.2. Because the half-lives are long relative to the time of the experiment, the insoluble products are believed to be the esters, which precipitate at high temperatures, and not the products caused by rapid decomposition.

6.8 Investigation of the kinetics of decomposition of fatty-alcohol ethoxylate esters of 4,4'-azobis-4-cyanopentanoic acid in water. In order to determine the rate coefficient, k_d, for the first-order decomposition of the fatty-alcohol ethoxylate esters of 4,4'-AB-4-CPA in water, an experiment was carried out in which the decomposition of the azo groups in the ethoxylate ester was followed using ultraviolet spectroscopy. The azo group in 4,4'-AB-4-CPA and the derivatives prepared in this investigation has a maximum absorption band in the ultraviolet region at approximately 350 nm. The decomposition of the azo compound was followed by observing the decrease in the height of this peak.

The initial optical density, D_o, was measured at the start of the experiment. The optical densities at different times, D_t, were also measured. Finally, complete decomposition of the azo group in the ester was accomplished by heating a sample at approximately 70^oC for two days in an oven. Ultraviolet spectroscopy revealed the absence of azo group in the sample after this treatment, since no further reduction in the optical density was observed after a further period at 70^oC. The optical densities of samples treated in this way are denoted by D_∞. Values of k_d were obtained from slopes of plots of log $[(D_o - D_\infty)/(D_t - D_\infty)]$ against

time. The results of these experiments are given in Figs. 6.23 - 6.26. The values obtained are summarised in Table 6.2.

The activation energy, F, was obtained using the usual formula,

$$k_d = A \exp(-F/RT)$$

where k_d is the rate constant, R is the gas constant (8.314 J mol^{-1} K^{-1}), and T is the absolute temperature. Values of F and A were obtained from a plot of log k_d versus 1/T, since

$$\log k_d = \log A - F/RT$$

The intercept of of log k_d versus 1/T gives the value of log A. The slope of log k_d versus 1/T yields F. The method of least squares was used in this work. These results are given in Figs. 6.27 - 6.30. The results show first-order decomposition rates.

6.9. Particle-size measurements.

6.9.1. Particle-size measurements on the final latices. Since emulsion polymerisation takes place in isolated loci, particle-size measurements were carried out in the hope that the results would throw some light on the mechanism of emulsion polymerisation of styrene when the fatty-alcohol ethoxylate esters were used as initiator/stabilisers. All the final latices obtained were subjected to particle-size measurements using the Coulter Nanosizer. The results of these experiments are given in Tables 6.3 - 6.7. The number of particles per litre of latex was calculated using the formula given in Chapter Five, section 5.7.5.4. It was assumed that ρ, the density of the polymer-monomer mixture, varied linearly with conversion. The value of ρ was taken as 0.905 g/cm^3 for styrene[157] and 1.05 g/cm^3 for polystyrene[157].

6.9.2. Particle-size measurements throughout the reaction. The information yielded by the experiments described in section 6.9.1 was incomplete in that particle-size measurements were made on the final latices only. For this reason, in some cases the variation in particle size

was followed as the reaction proceeded. The particle-size measurements were carried out using (i) a Coulter Nanosizer and (ii) an electron microscope.

All the reactions were carried out using 1.1×10^{-3} mol of ester per 40 ml of styrene. The volume ratio of styrene to water was 40:100. Five reaction systems were used in these experiments, the details being as follows:

Initiator/stabiliser	Temperature (^{0}C)
$FA(FO)_{24}Fs$	60
$FA(FO)_{30}Fs$	60
$FA(FO)_{30}Fs$	40
$FA(FO)_{60}Fs$	60
$FA(FO)_{60}Fs$	40

Because the latices were in general very polydisperse, approximately 500 particles were measured when using electron microscopic techniques, in order to find the average diameter of a particle for a given latex at a given time of the reaction. Polydispersity is defined as D_w/D_v, where D_w is the weight-average diameter and D_v is the volume-average diameter:

$$D_w = \sqrt{\frac{\Sigma n_i d_i^{\,6}}{\Sigma n_i d_i^{\,3}}}$$

$$D_v = \sqrt{\frac{\Sigma n_i d_i^{\,3}}{\Sigma n_i}}$$

The results are given in Tables 6.8 - 6.12.

6.10. Molecular weight determinations. The molecular weights of the polystyrenes obtained using these initiator/stabilisers were determined at RAPRA by Dr. S. Holding. Previously, the writer had attempted to use viscometry to determine the molecular weight of polystyrene obtained when 1.1×10^{-3} mol of $FA(FO)_{24}Fs$ was used as initiator/stabiliser; the temperature of the reaction was 50^{0}C and the volume ratio of styrene to water was 40:100. The weight-average molecular weight found was above 10^6. It was felt that viscometry was not suitable method for this range of

molecular weight. Thus, the molecular weights (given as M_n and M_w, where M_n is the number-average molecular weight and M_w the weight-average molecular weight), and also $D = M_n/M_w$, were obtained at RAPRA by gel-permeation chromatography. As can be seen from the enclosed examples, the high-molecular-weight shoulder present is thought to be material of larger molecular weight than the capacity of the columns used. The calculations were carried out using the trace from a differential refractive index detector. The results are shown in Table 6.15 and Figs. 6.31 and 6.32.

A new set of experiments was carried out using high-molecular-weight calibration (Figs. 6.33 and 6.34. This calibration covers the range from 400,000 to 5,000,000 (Fig. 6.35). According to Dr. Holding, outside this range, the molecular weights were determined by extrapolation of the polynomial (third-order calibration). Dr. Holding also attempted to verify some of the values for the weight-average molecular weights M_w, using low-angle laser light scattering. These results are given in Table 6.14.

6.11. Bulk polymerisations of styrene using the fatty-alcohol ethoxylate esters. Finally, the efficiency of the fatty-alcohol ethoxylate esters as initiators for the bulk polymerisation of styrene was investigated. The formulation employed was 40 ml of styrene plus 1.1×10^{-3} mol of ester. The styrene and the ester were placed in a test tube; nitrogen was bubbled through, and the test tube was then stoppered. The test tube was placed in a water bath for six hours at $50^{o}C$. The polymer was precipitated using 150 ml of methanol to which tert-butylcatechol had been added. Table 6.15 shows the results obtained. The same recipe and procedure were used in control experiments using AZBN as initiator. This result is also given in Table 6.15.

Compound	Room Temp	40°C	50°C	55°C	60°C	70°C	75°C	80°C	Approx. cloud point
$FA(EO)_2Es$	insol	insol	insol	insol	insol	insol	insol	insol	-----
$FA(EO)_6Es$	insol	insol	insol	insol	insol	insol	insol	insol	-----
$FA(EO)_{10}Es$	insol	insol	insol	insol	insol	insol	insol	insol	-----
$FA(EO)_{14}Es$	sol (cloudy)	sol	sol	part sol	insol	insol	insol	insol	55°C
$FA(EO)_{24}Es$	sol	sol	sol	sol	sol	part sol	insol	insol	70°C
$FA(EO)_{30}Es$	sol	sol	sol	sol	sol	sol	part sol	insol	75°C
$FA(EO)_{45}Es$	sol	sol	sol	sol	sol	sol	sol	sol	> 80°C
$FA(EO)_{60}Es$	sol	sol	sol	sol	sol	sol	sol	sol	> 80°C

Table 6.1. Effect of temperature on the water solubility of the initiator/stabiliser. Approximate cloud points.

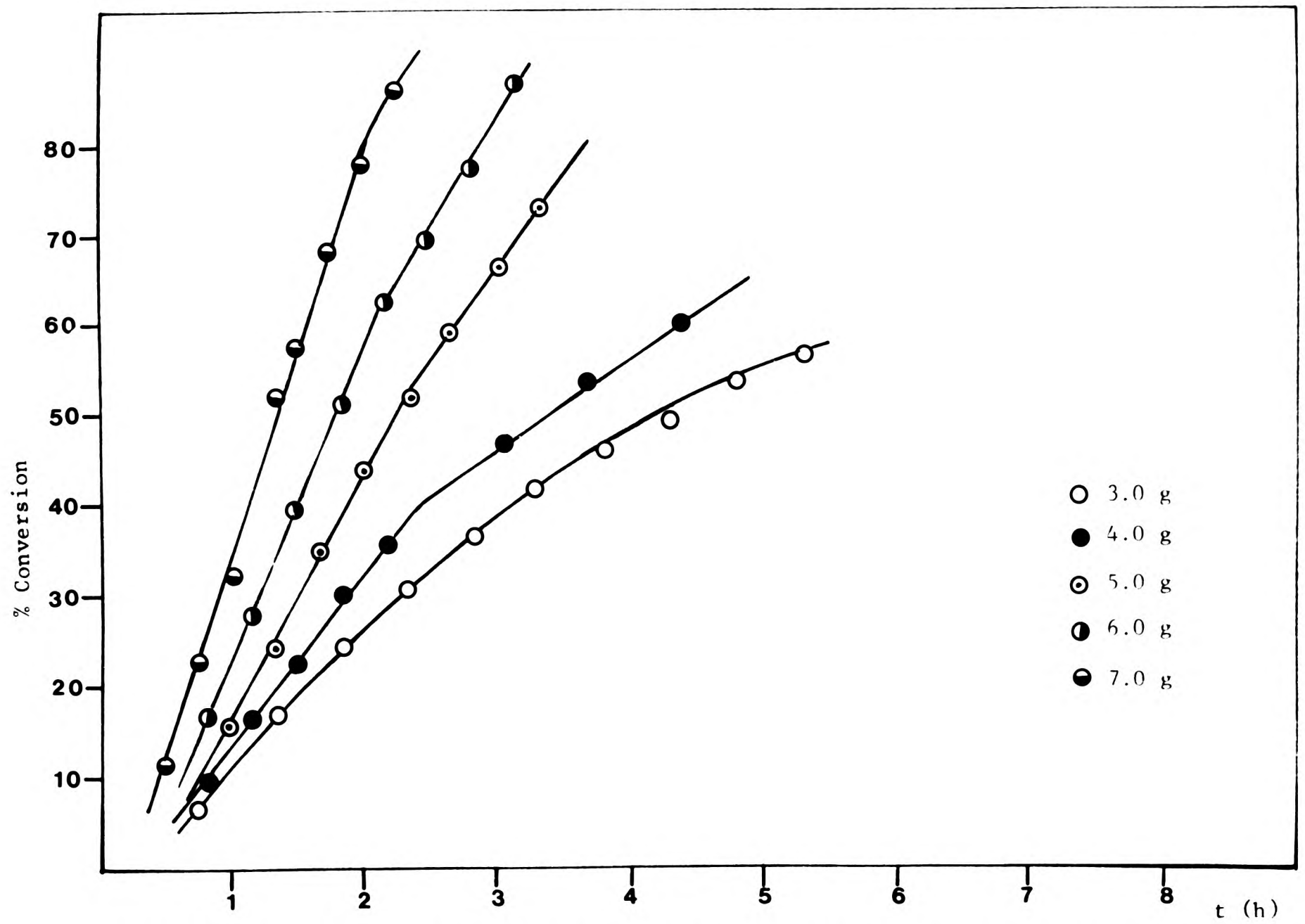


Fig. 6.5: Effect upon the emulsion polymerisation of styrene of varying the mass of initiator $FA(EO)_{24}Es$ at $50^{o}C$.

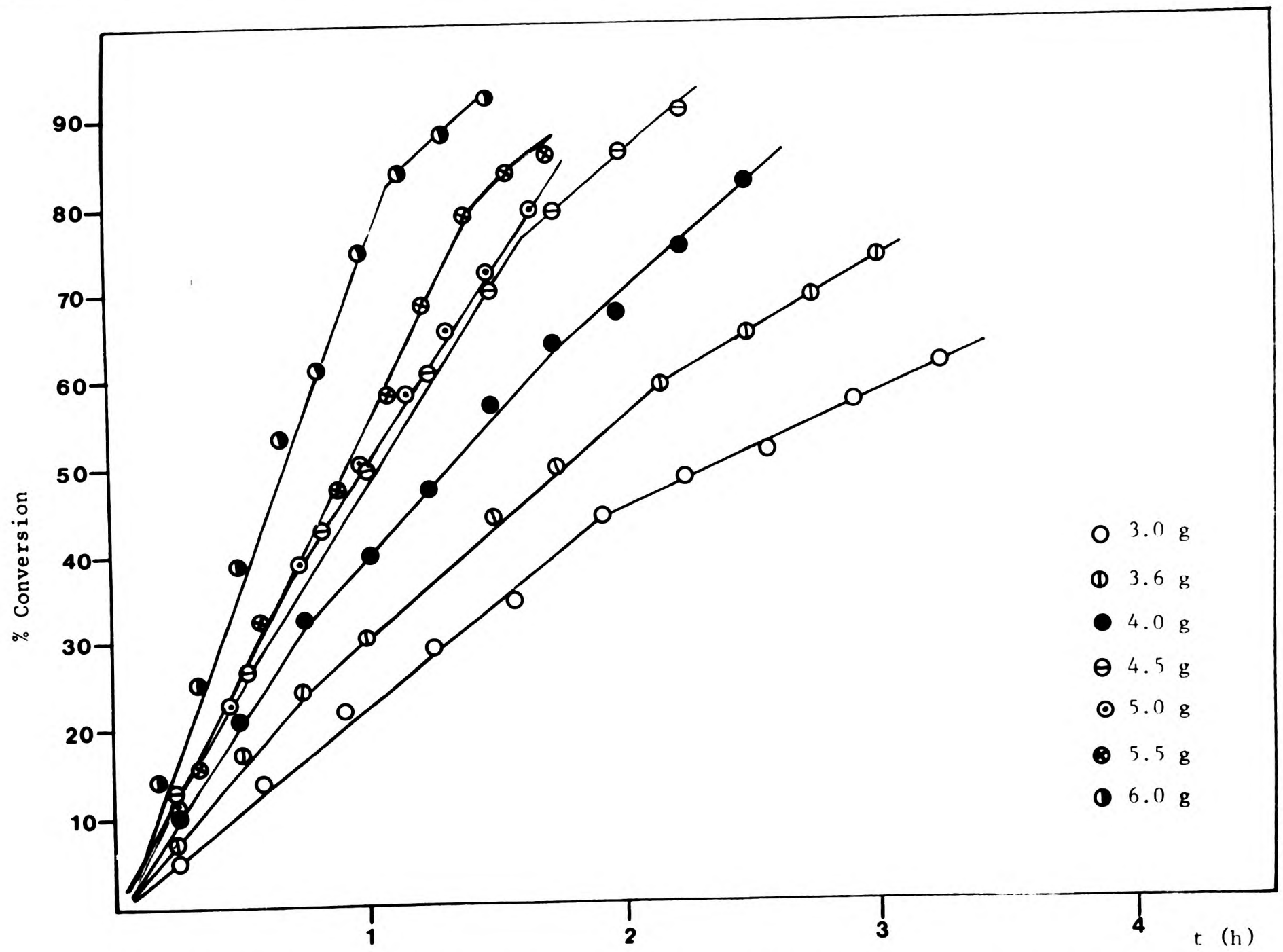


Fig. 6.6: Effect upon the emulsion polymerisation of styrene of varying the mass of initiator $FA(EO)_{30}Es$ at 50°C.

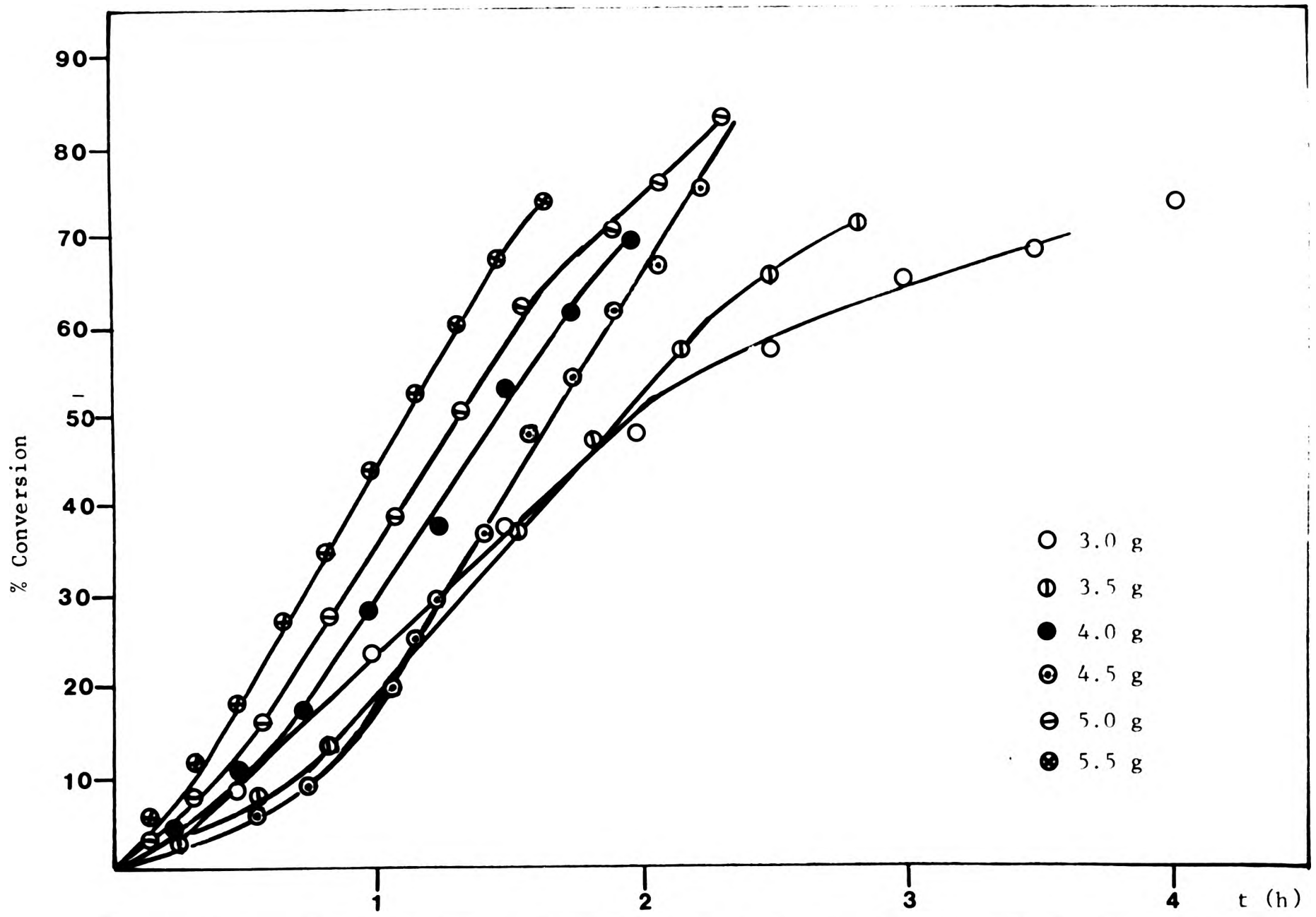


Fig. 6.7: Effect upon emulsion polymerisation of styrene of varying the mass of initiator $FA(EO)_{45}Es$ at 50°C.

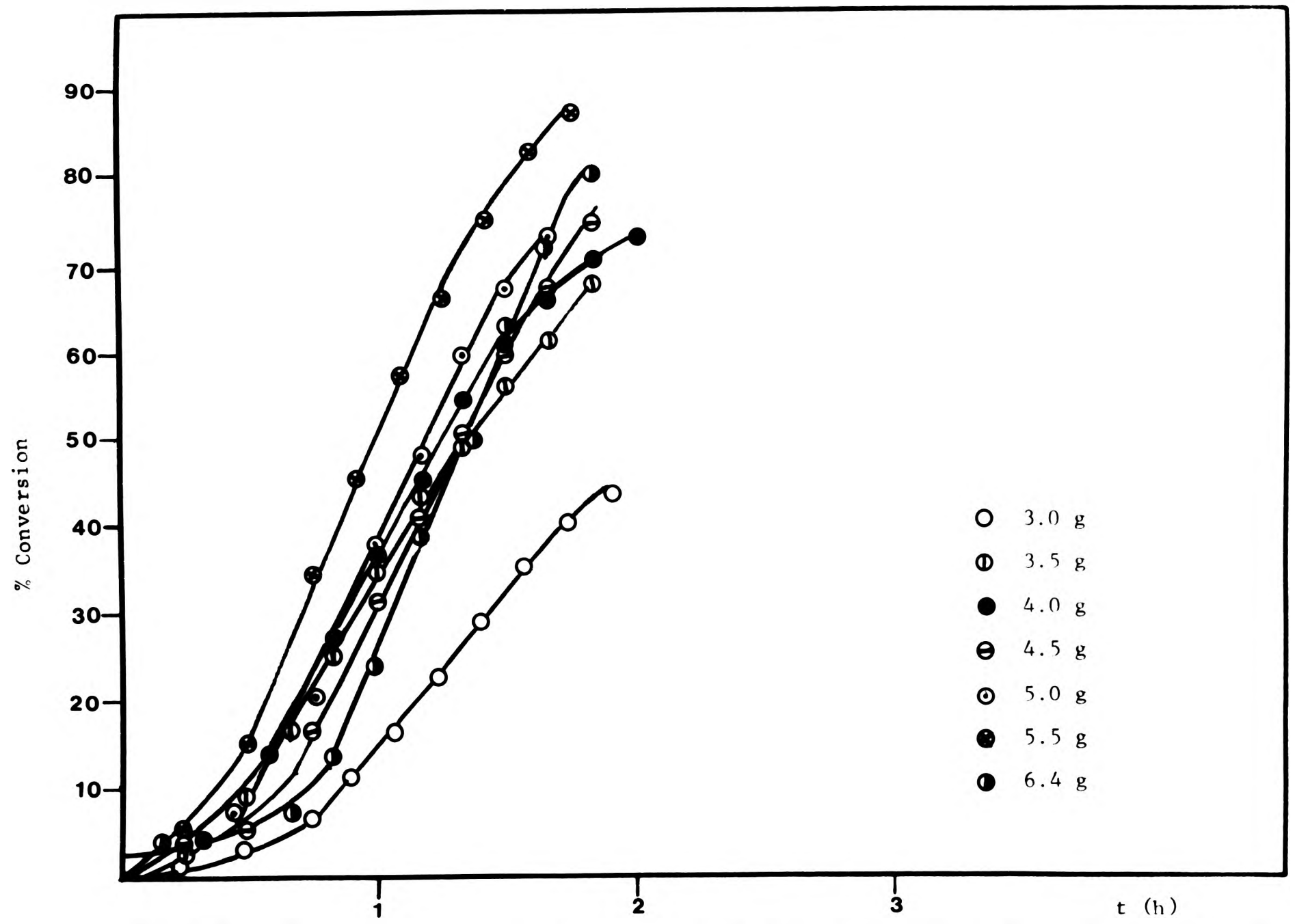


Fig. 6.8: Effect upon emulsion polymerisation of styrene of varying the mass of initiator $FA(EO)_{60}Es$ at $^{o}50$ C.

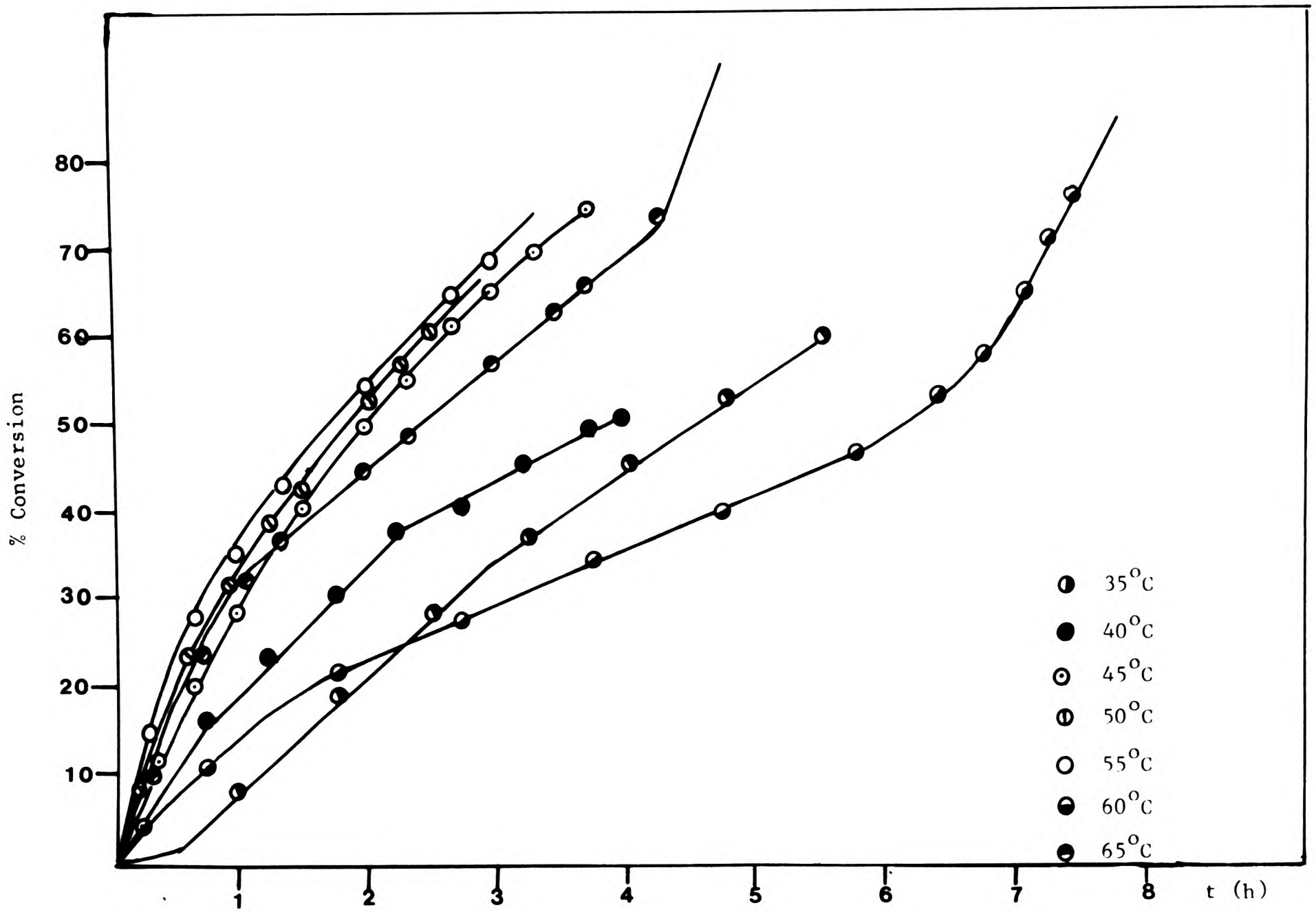


Fig. 6.9: Effect of temperature upon emulsion polymerisation of styrene using a constant molar amount (1.1×10^{-3} mol) of $FA(EO)_{24}Es$.

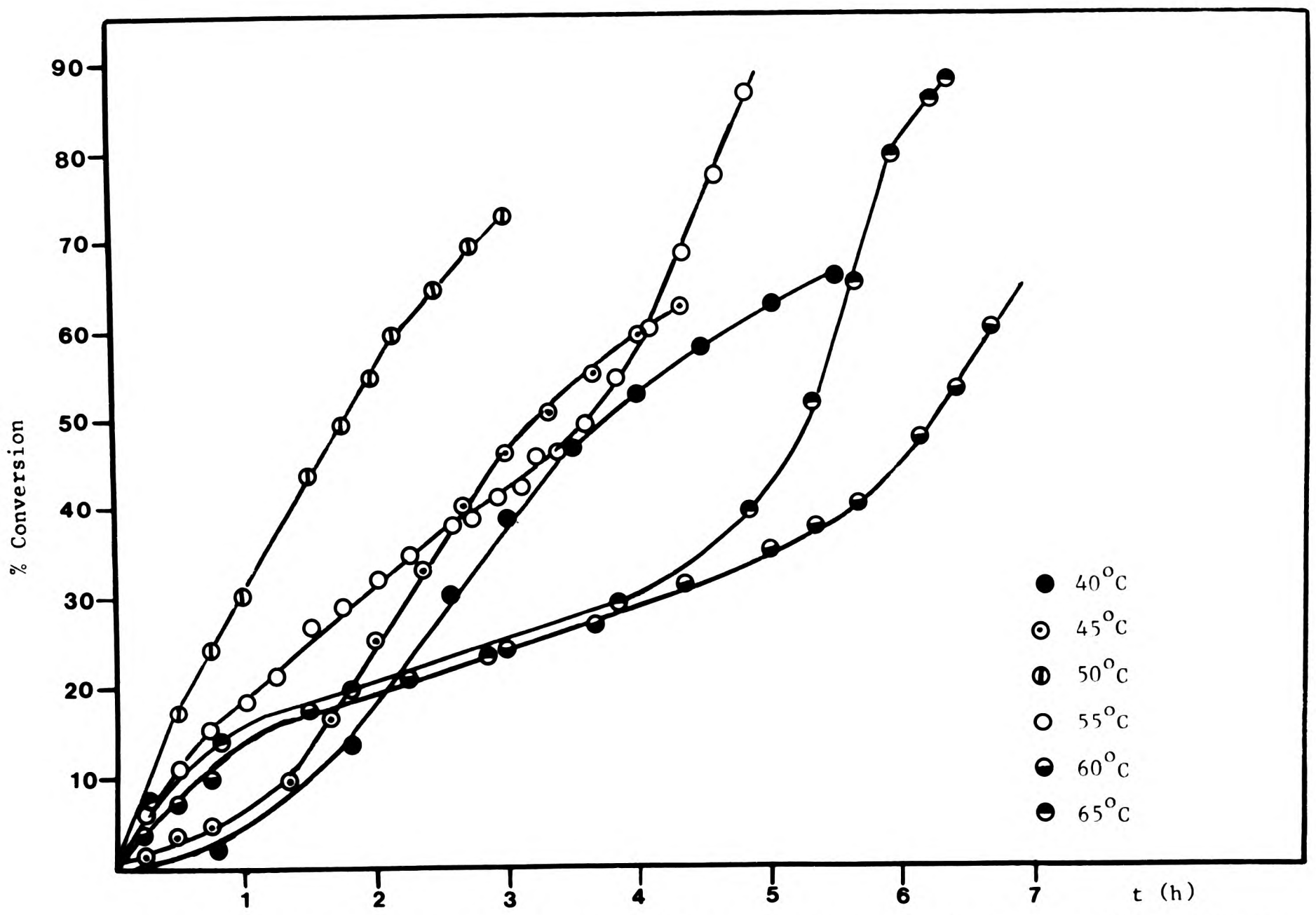


Fig. 6.10: Effect of temperature upon emulsion polymerisation of styrene using a constant molar amount (1.1×10^{-3} mol) of $FA(EO)_{30}Es$.

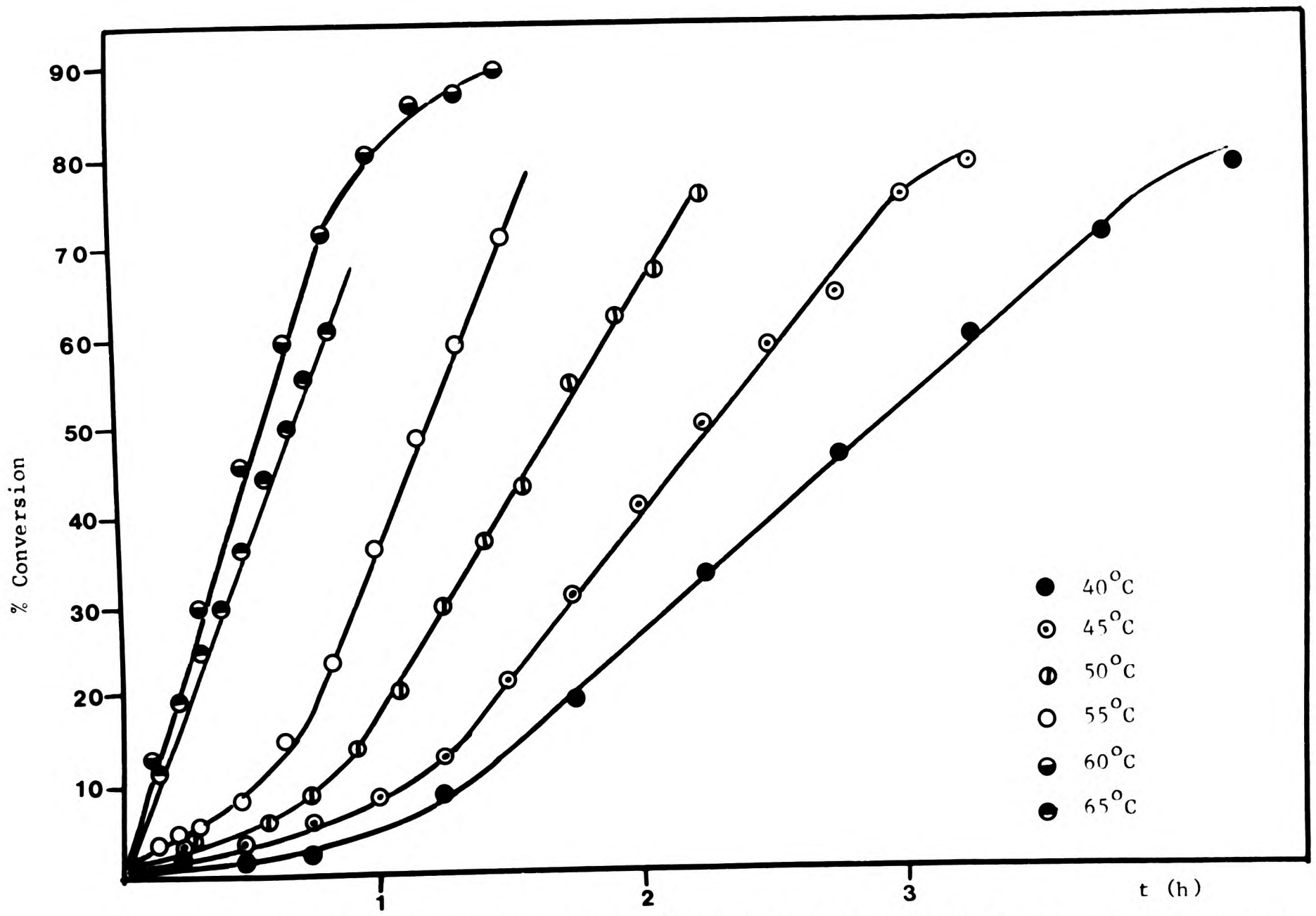


Fig. 6.11: Effect of temperature upon emulsion polymerisation of styrene using a constant molar amount (1.1×10^{-3} mol) of $FA(EO)_{45}Es$.

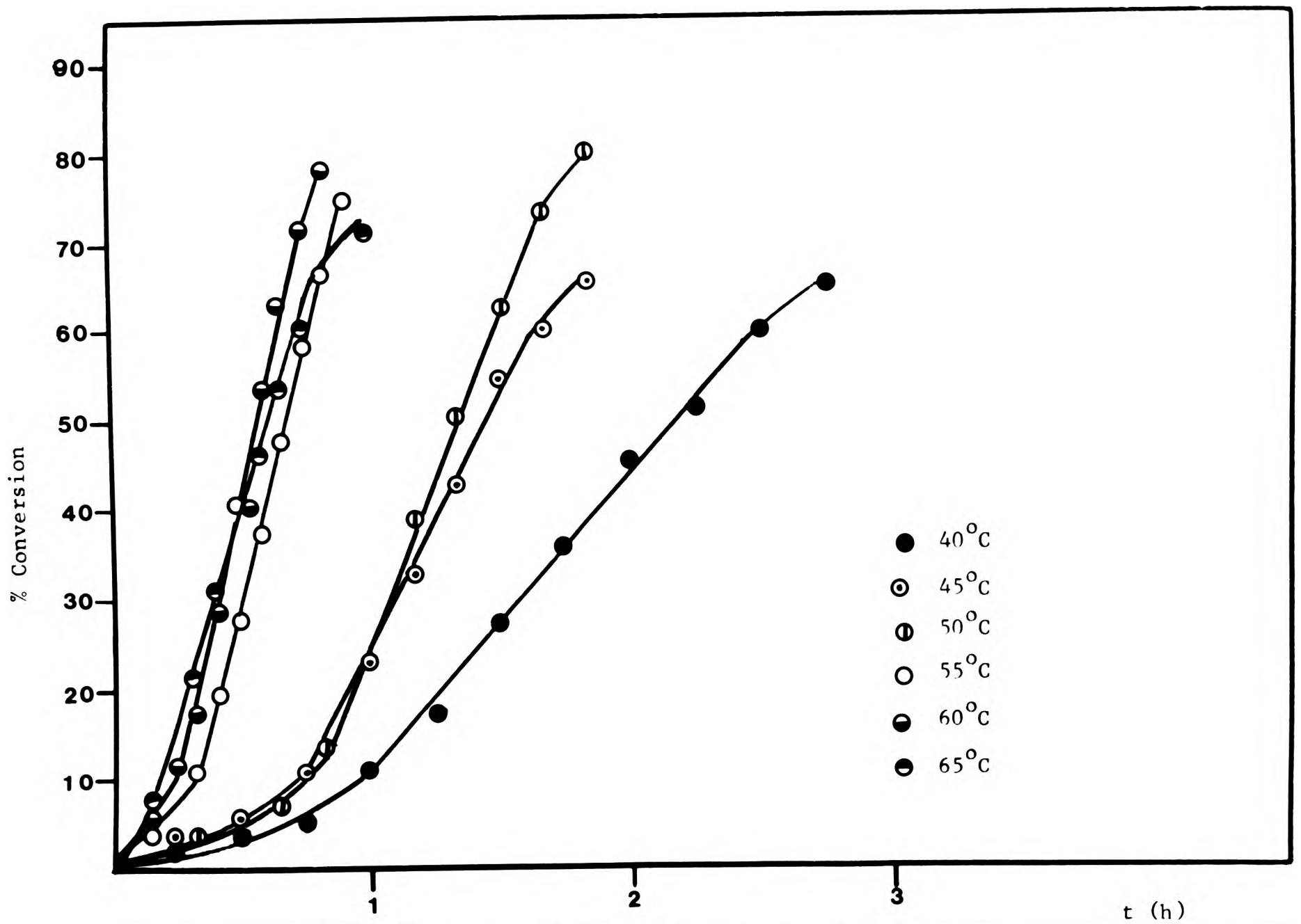


Fig. 6.12: Effect of temperature upon emulsion polymerisation of styrene using a constant molar amount (1.1×10^{-3} mol) of $FA(EO)_{60}Es$.

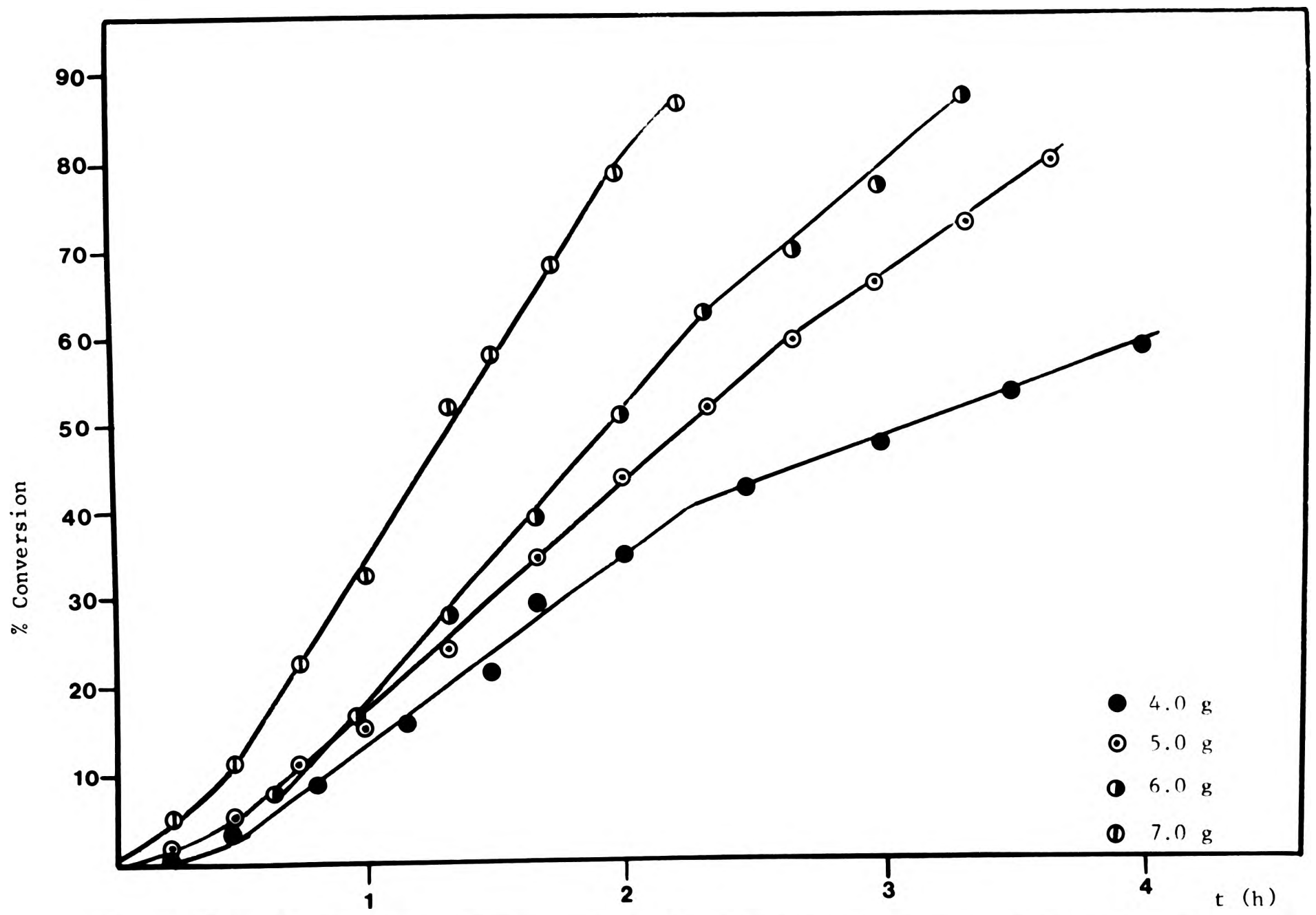


Fig. 6.13: Effect upon emulsion polymerisation of styrene of varying the mass of initiator $FA(EO)_{24}Es$ at $45^{o}C$.

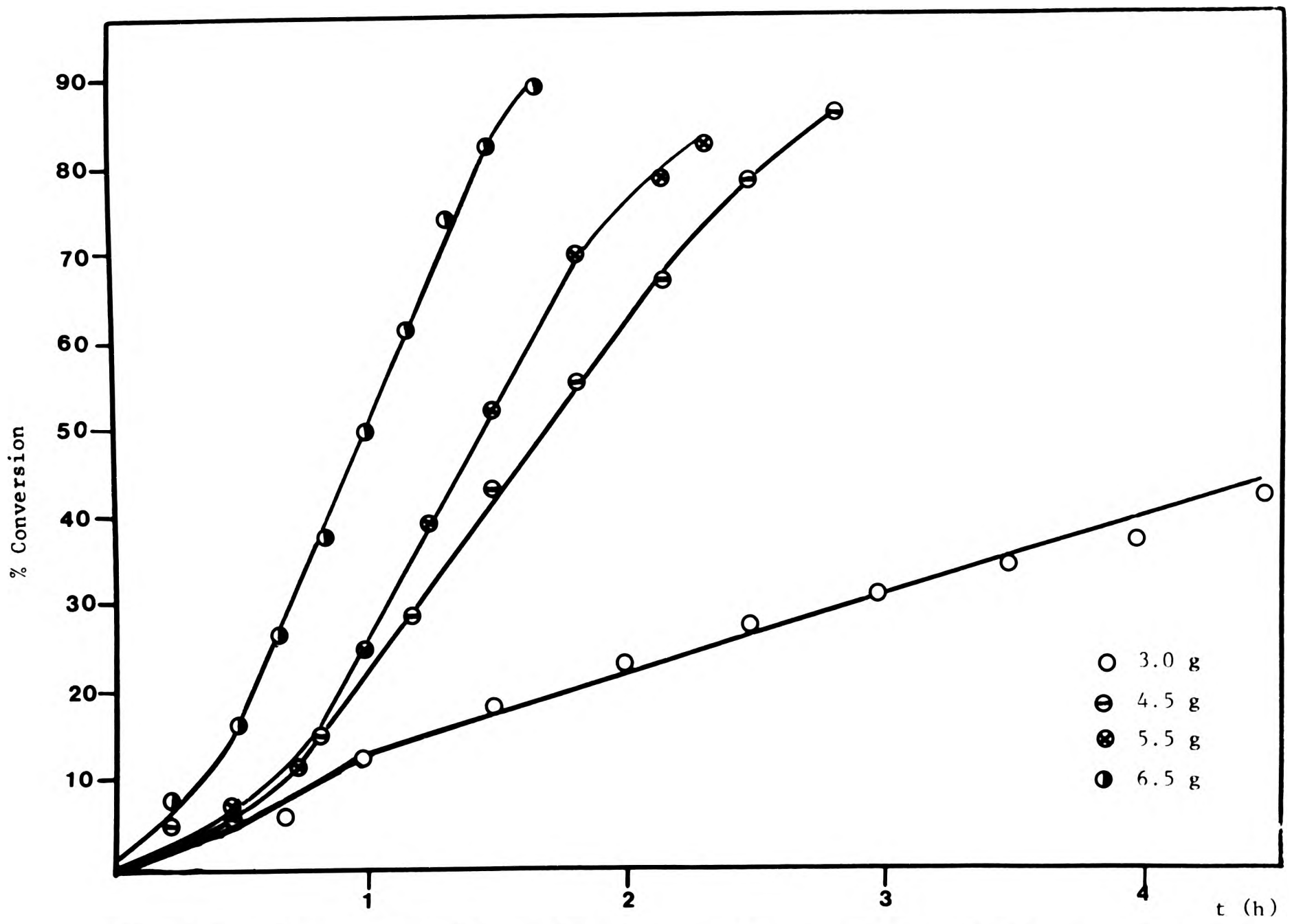


Fig. 6.14: Effect upon emulsion polymerisation of styrene of varying the mass of initiator $FA(EO)_{30}Es$ at 45°C.

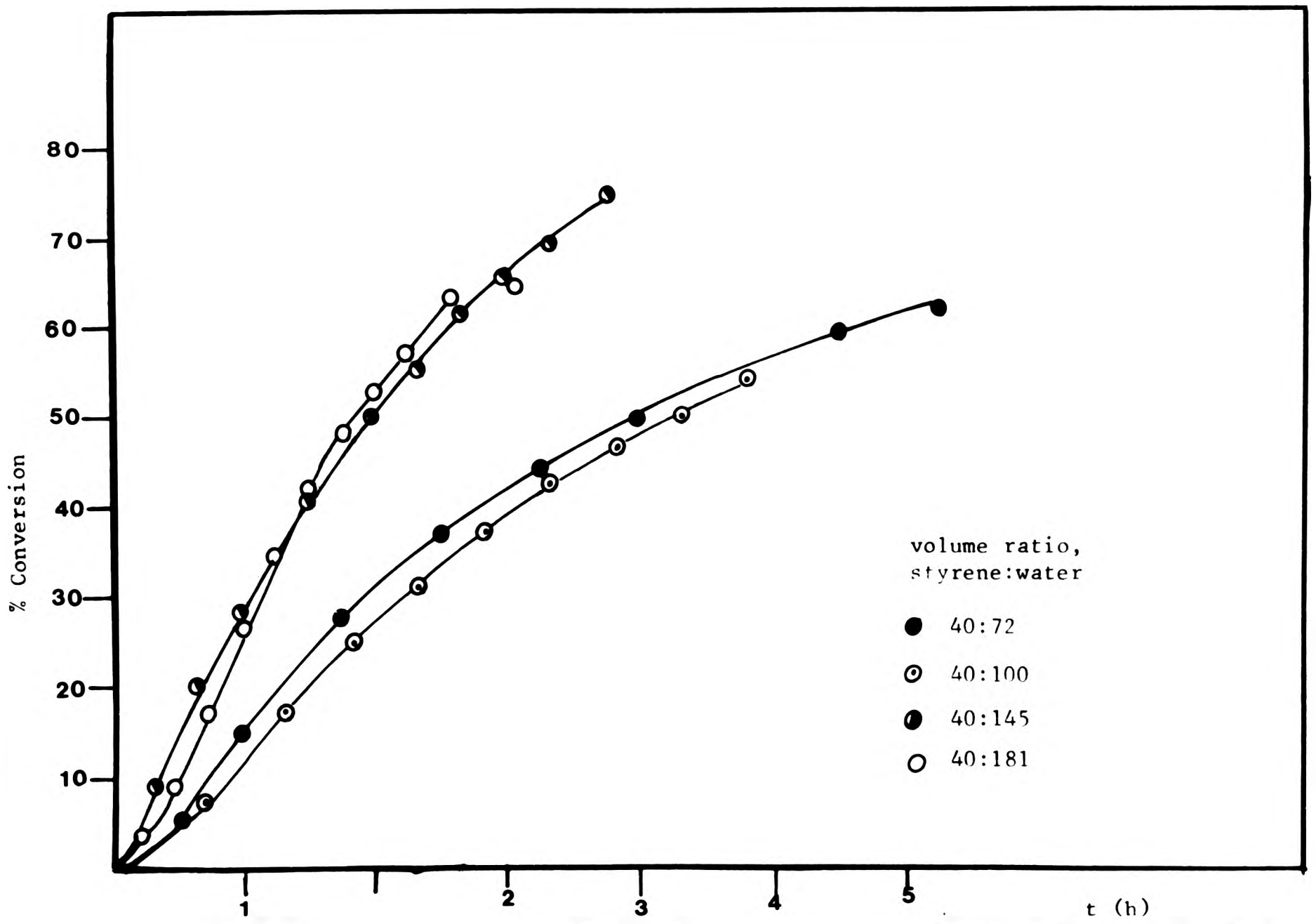


Fig. 6.15: Effect upon emulsion polymerisation of styrene of varying the volume of water using a constant molar amount (1.1×10^{-3} mol) of $FA(EO)_{24}Es$ at 45°C.

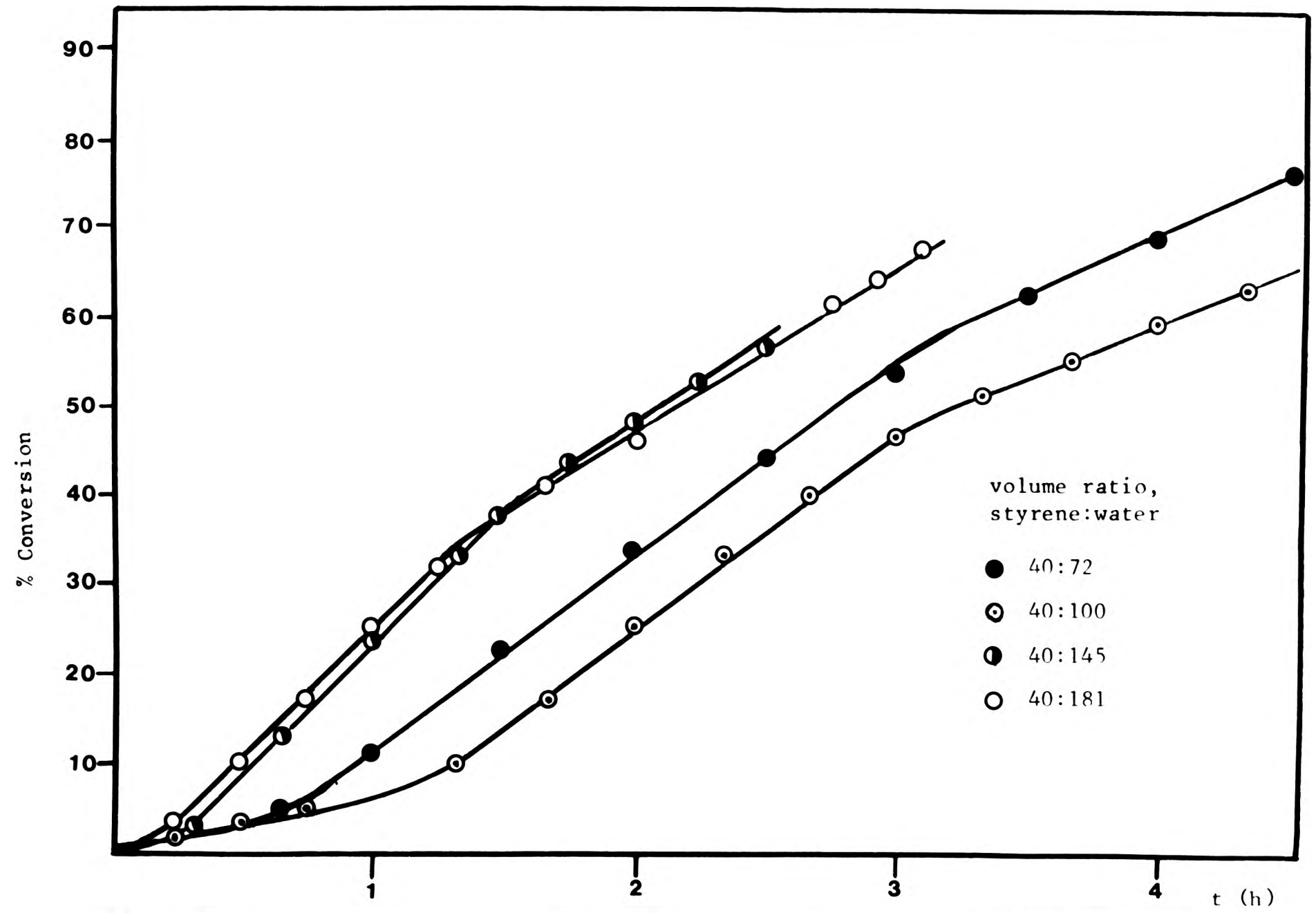


Fig. 6.16: Effect upon emulsion polymerisation of styrene of varying the volume of water using a constant molar amount (1.1×10^{-3} mol) of $FA(EO)_{30}Es$ at 45°C.

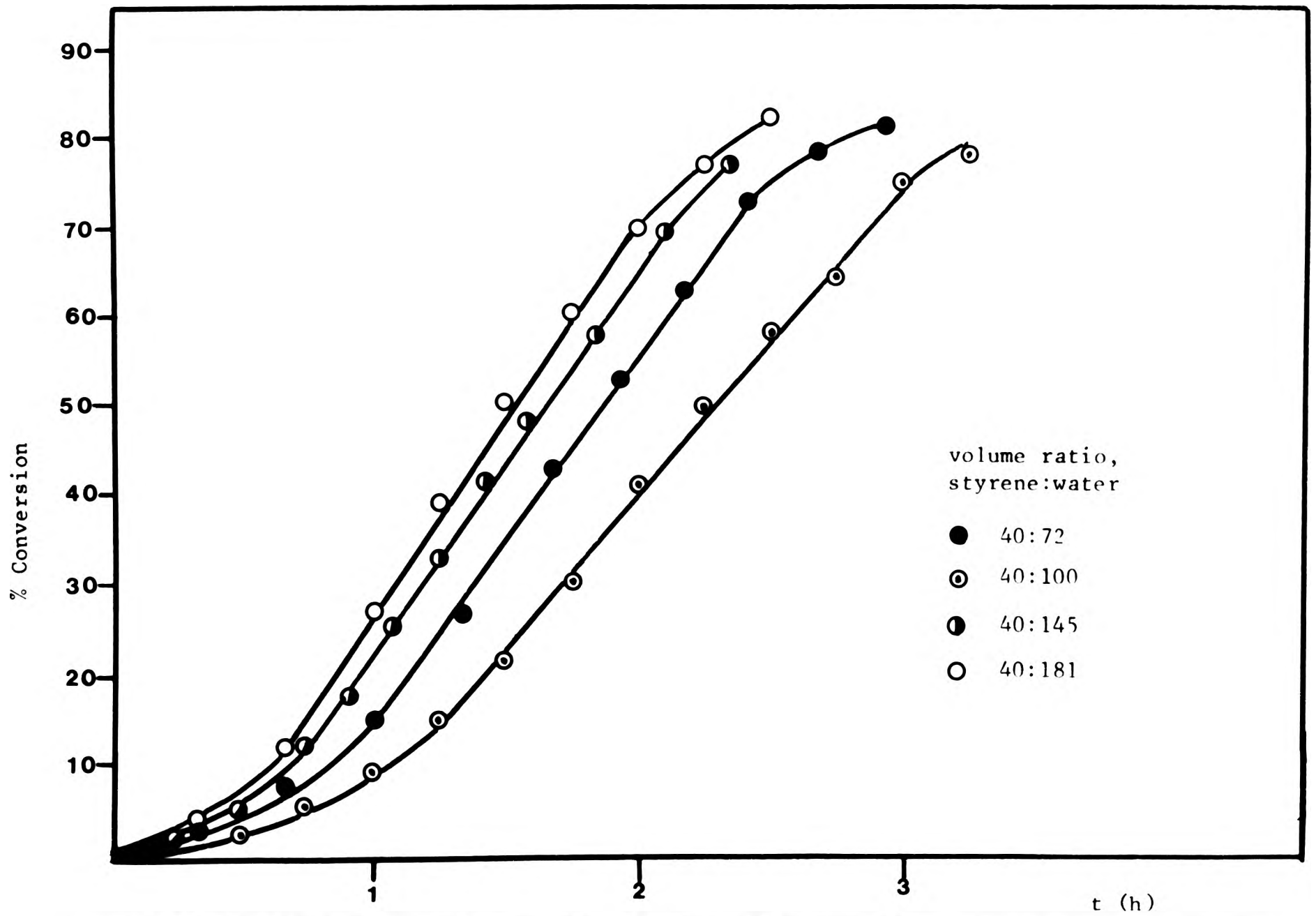


Fig. 6.17: Effect upon emulsion polymerisation of styrene of varying the volume of water using a constant molar amount (1.1×10^{-3} mol) of $FA(EO)_{45}Es$ at $45^{o}C$.

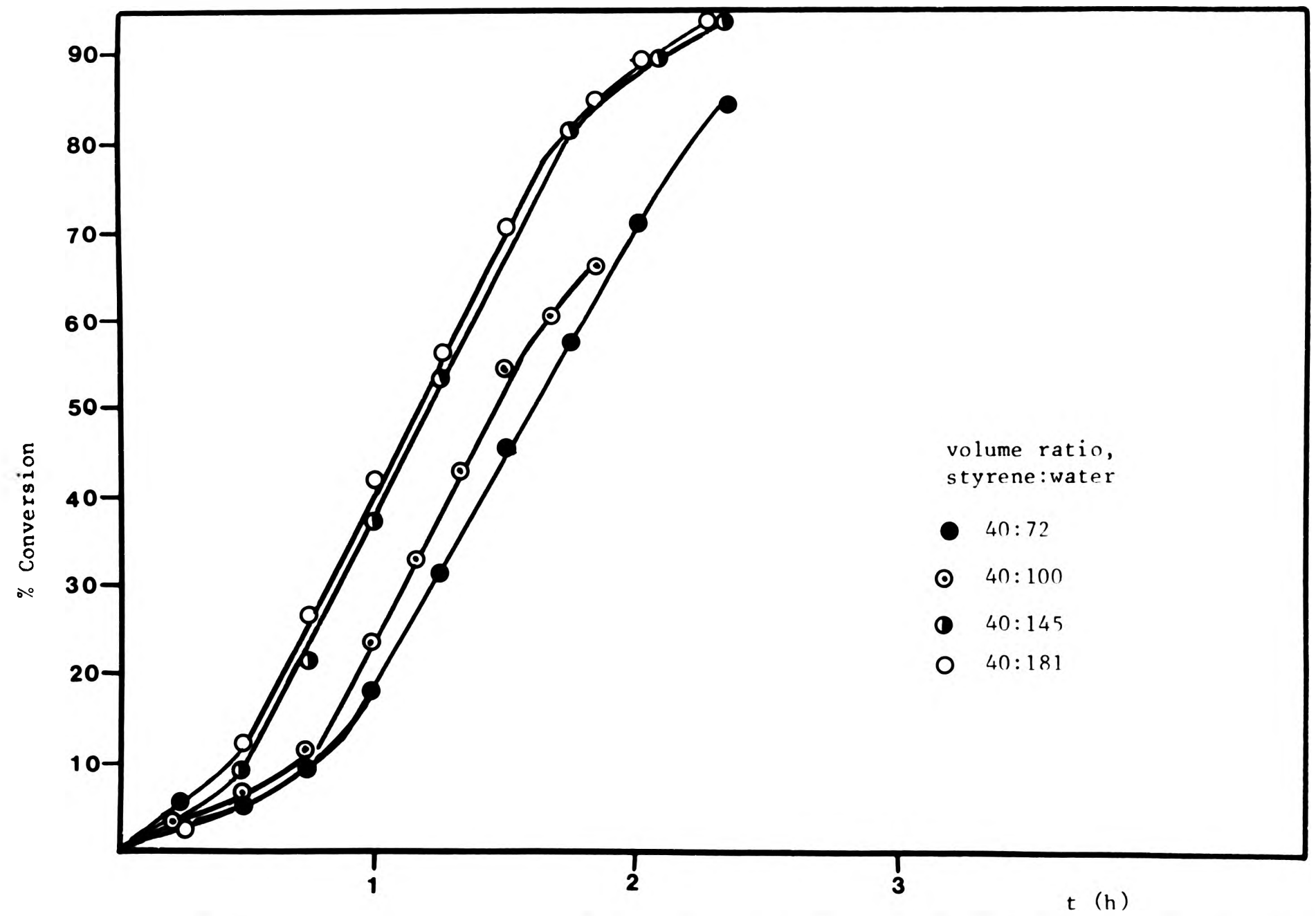


Fig. 6.18: Effect upon emulsion polymerisation of styrene of varying the volume of water using a constant molar amount (1.1×10^{-3} mol) of $FA(EO)_{60}Es$ at 45°C.

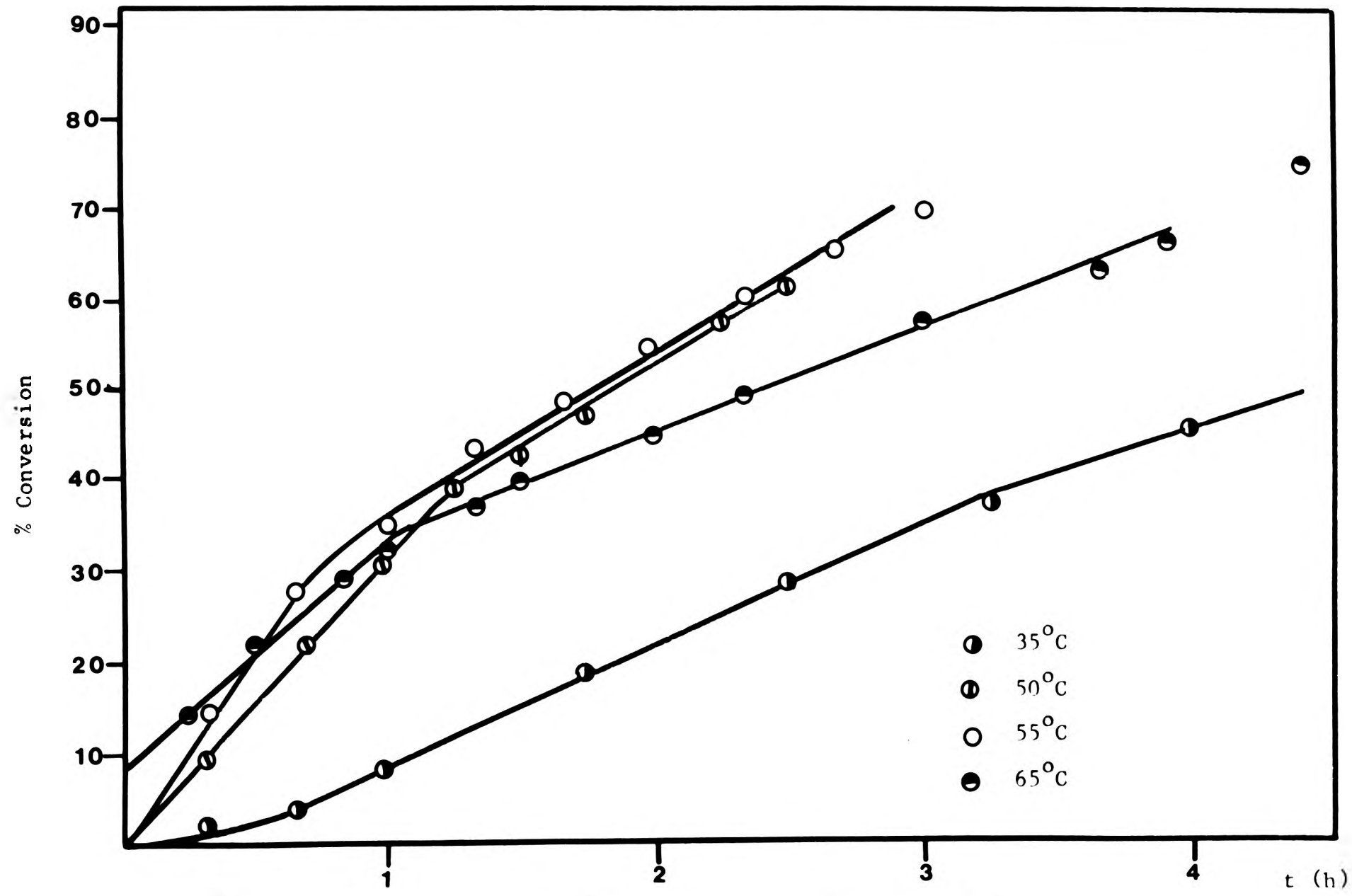


Fig. 6.19: Effect upon emulsion polymerisation of styrene of varying the temperature using a constant molar amount (1.1×10^{-3} mol) of $FA(EO)_{24}Es$ and a water:styrene ratio of 145 ml:40 ml.

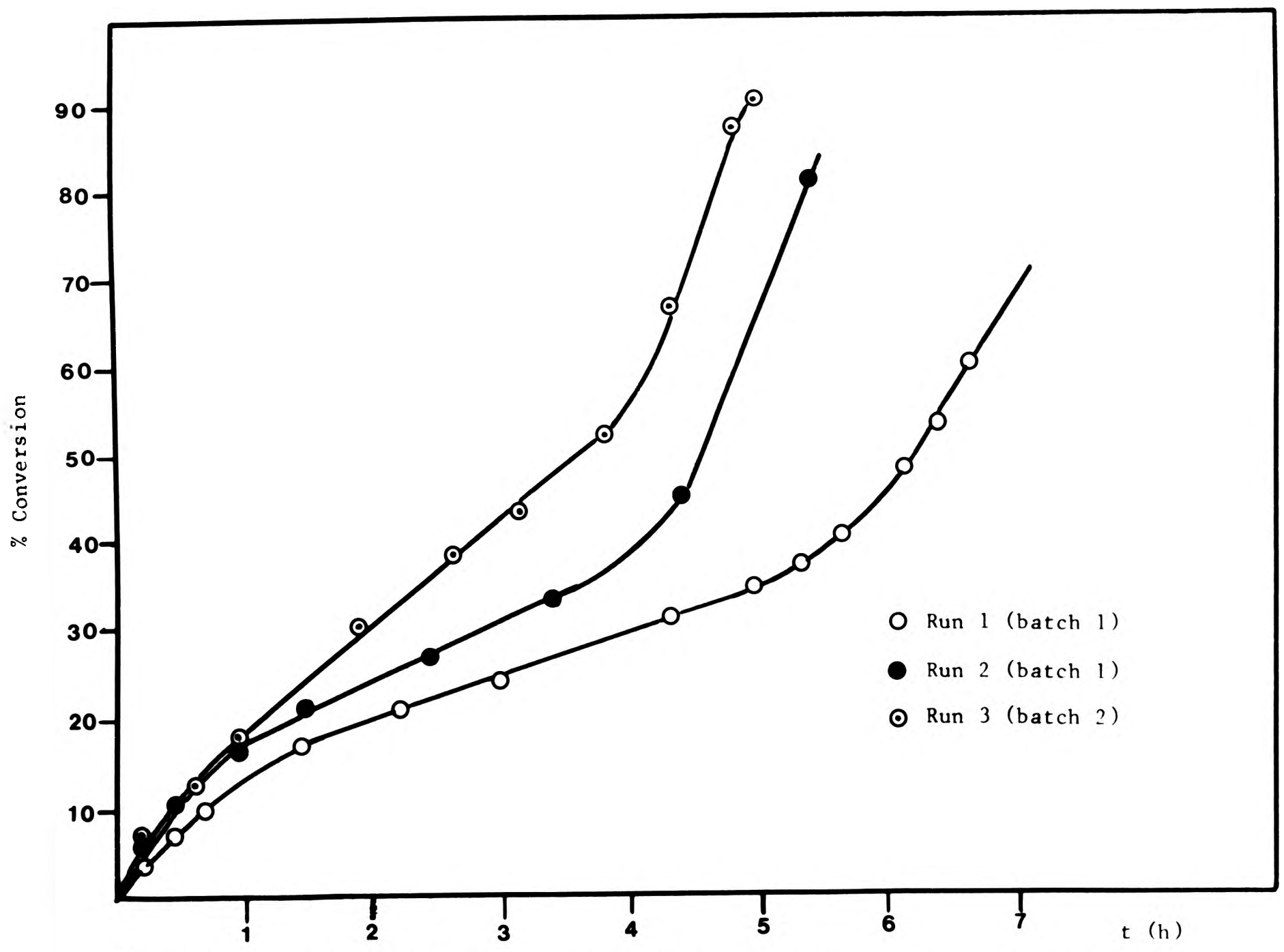


Fig. 6.20: Reproducibility of conversion-time curve obtained using $FA(EO)_{30}Es$ as initiator/stabiliser at $60^{o}C$.

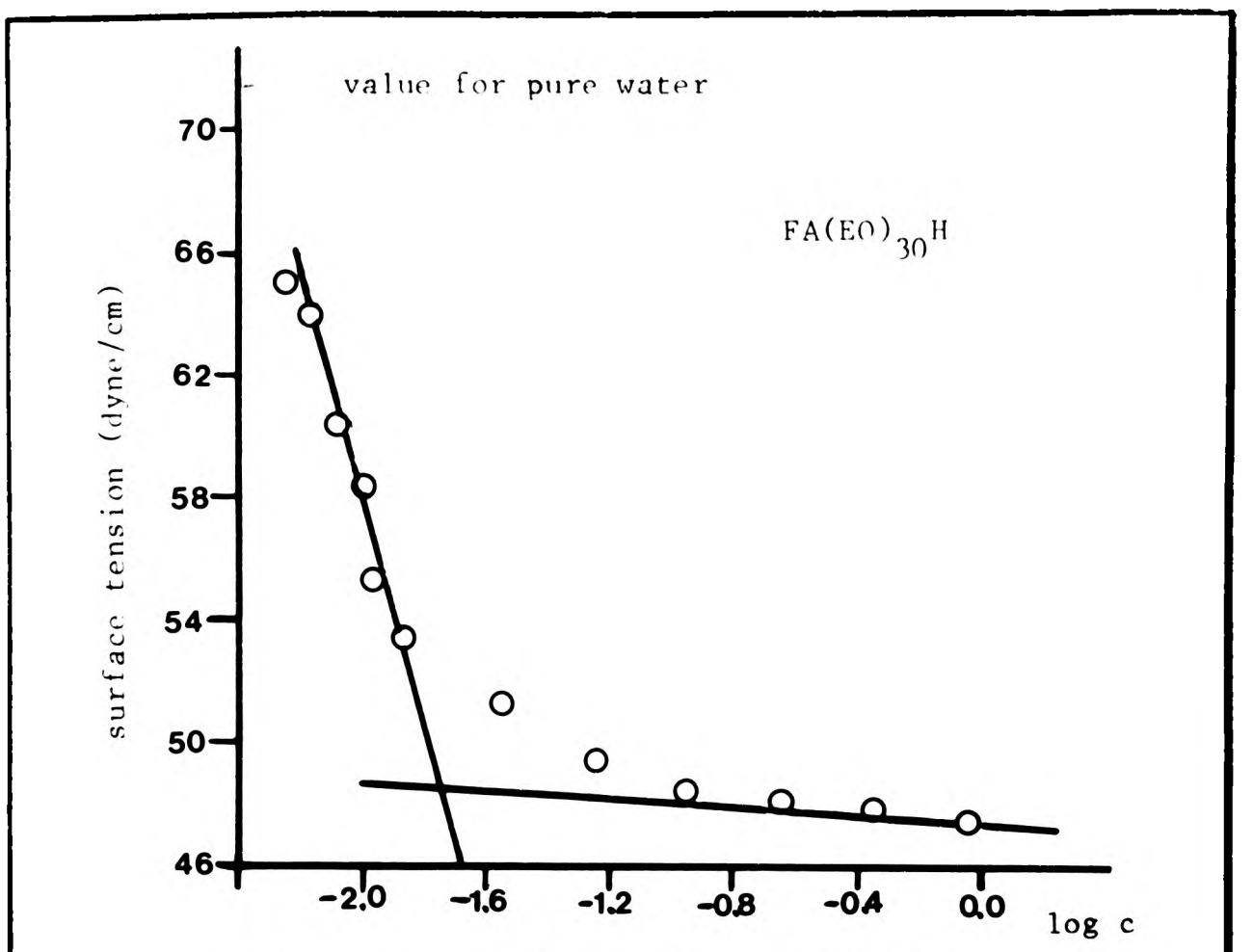


Fig. 6.21a: Surface tension measurements

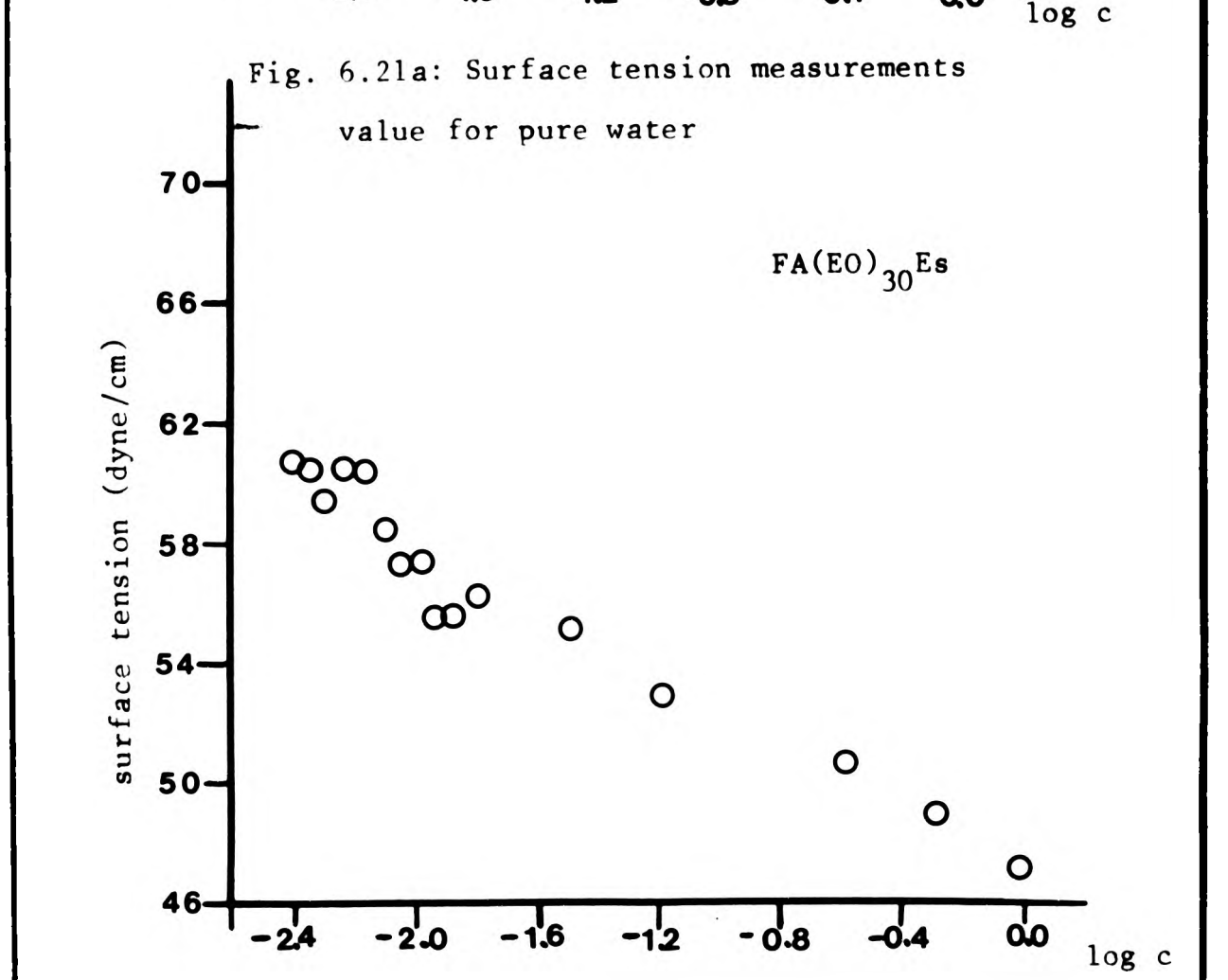


Fig. 6.21b: Surface tension measurements

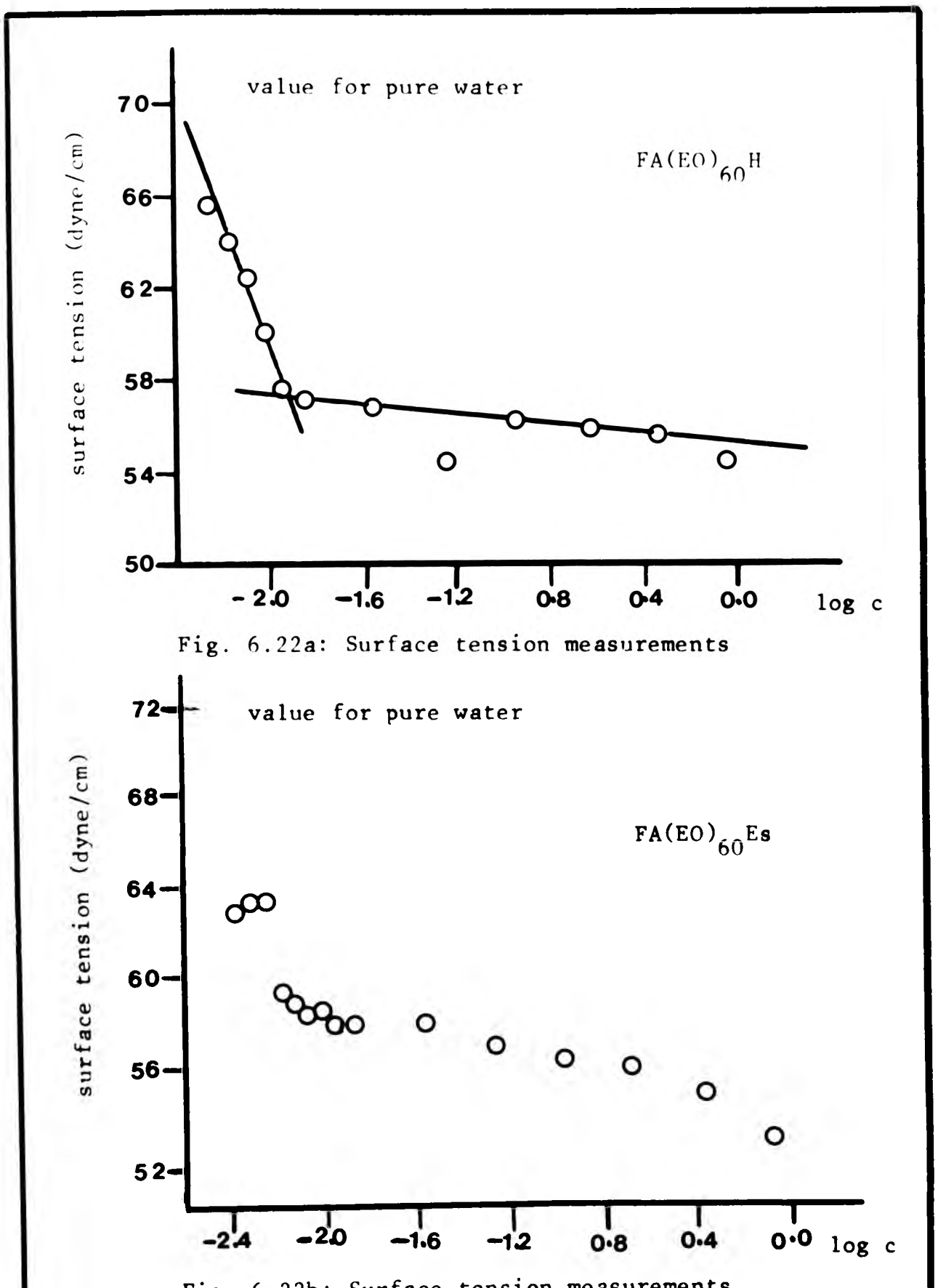
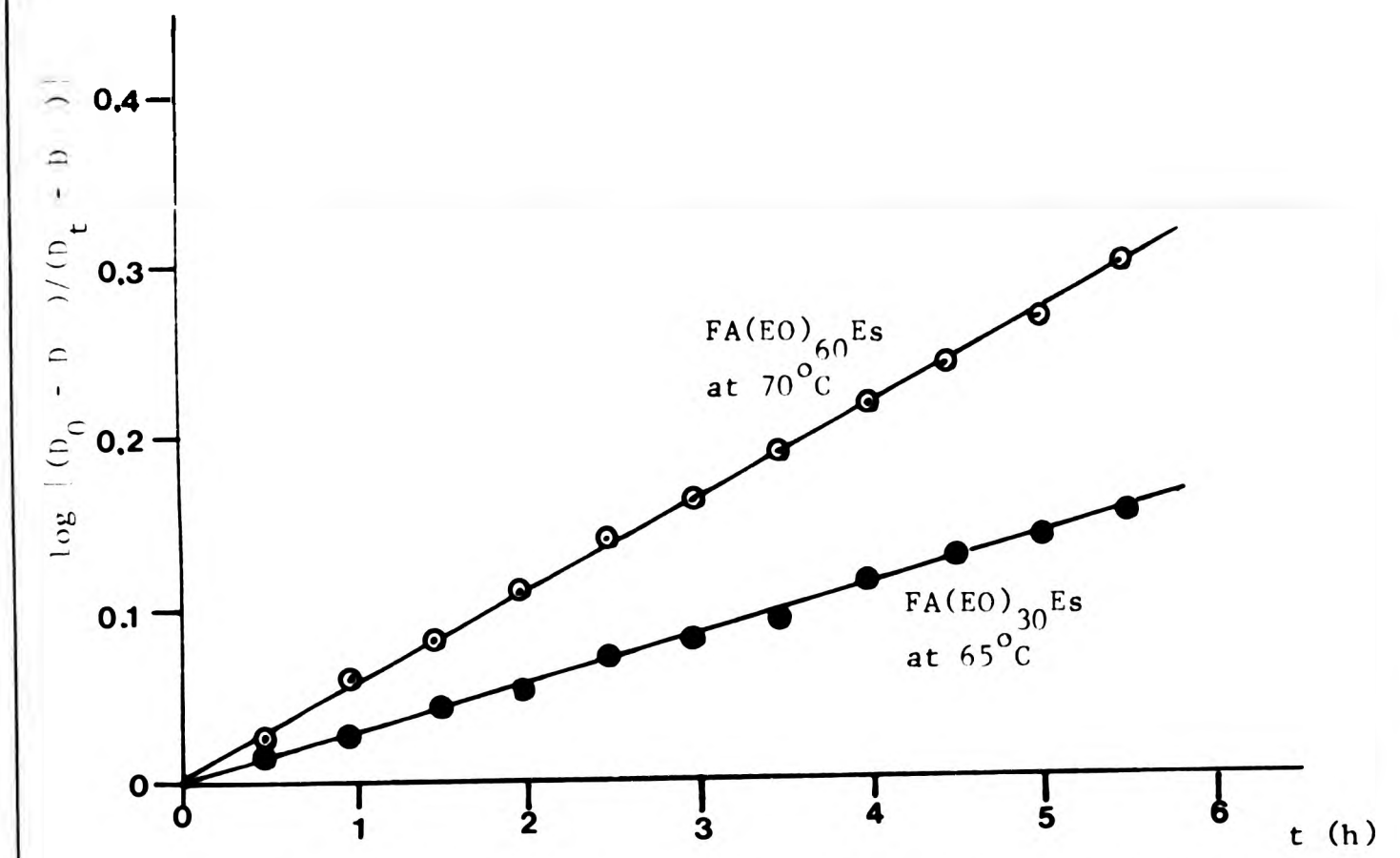
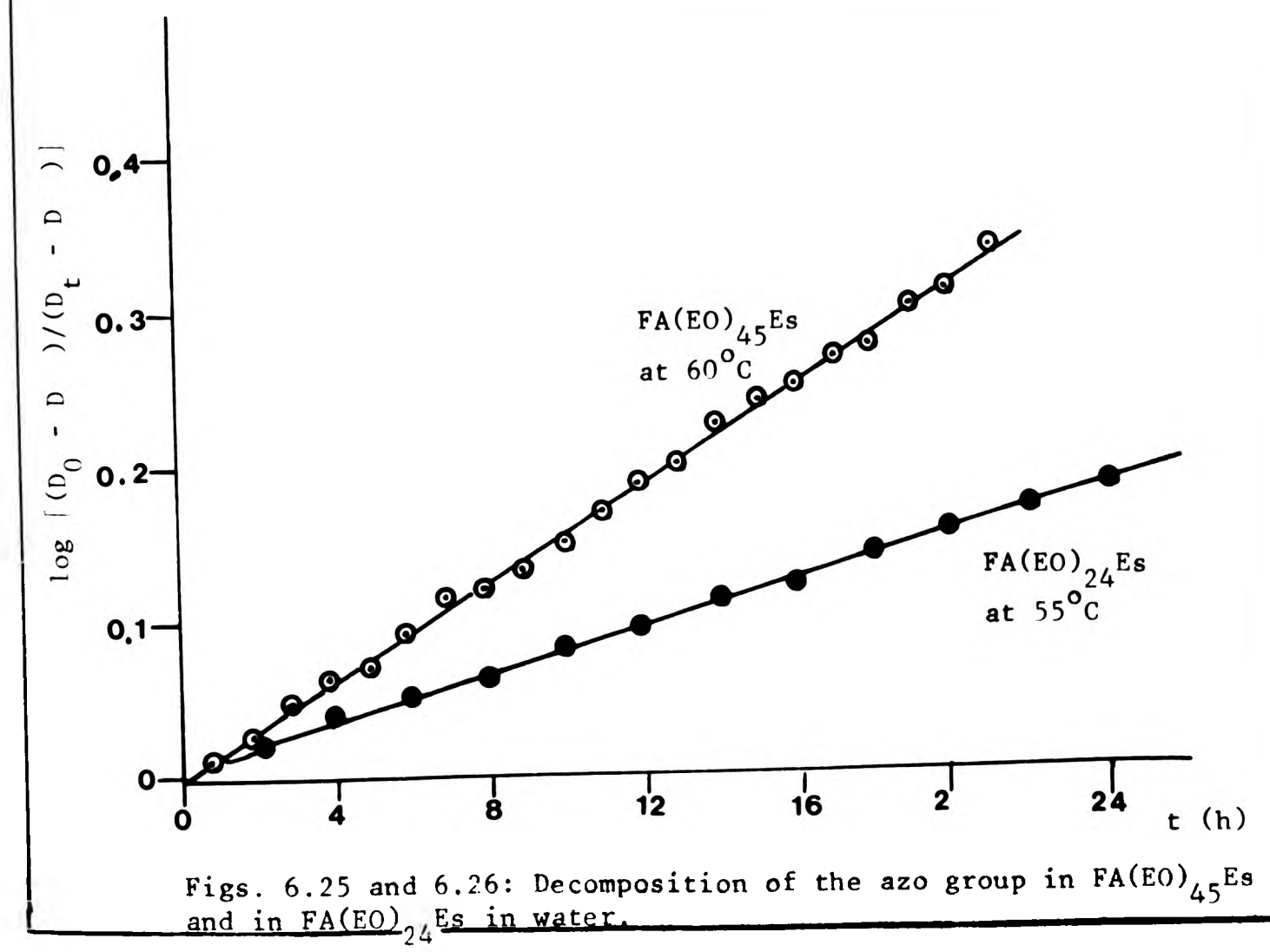


Fig. 6.22a: Surface tension measurements

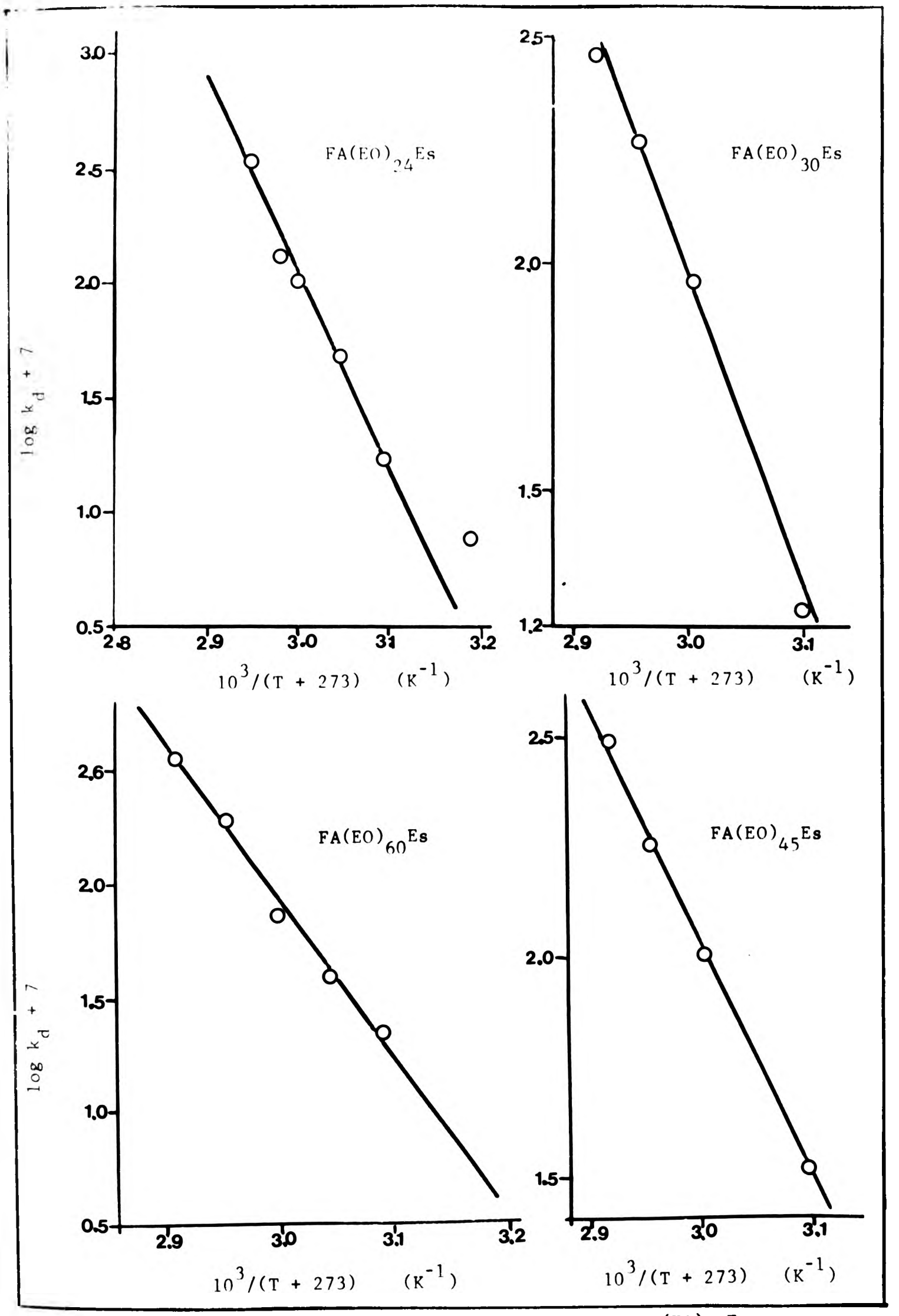
Fig. 6.22b: Surface tension measurements



Figs. 6.23 and 6.24: Decomposition of the azo group in $FA(EO)_{60}Es$ and in $FA(EO)_{30}Es$ in water.



Figs. 6.25 and 6.26: Decomposition of the azo group in $FA(EO)_{45}Es$ and in $FA(EO)_{24}Es$ in water.



Figs. 6.27-6.30: Arrhenius plots obtained for $FA(EO)_{24}Es$, $FA(EO)_{30}Es$, $FA(EO)_{45}Es$ and $FA(EO)_{60}Es$.

Temperature (°C)	k_d (s^{-1})	$t_{1/2}$ (h)
40	7.99×10^{-7}	241
50	1.74×10^{-6}	111
55	4.83×10^{-6}	39.9
60	1.04×10^{-5}	18.5
63	1.32×10^{-5}	14.6
66	3.41×10^{-5}	5.65

Table 6.2a: Rate coefficients for decomposition of the azo group in $FA(EO)_{24}Es$ in water.

Temperature	k_d (s^{-1})	$t_{1/2}$ (h)
50	1.76×10^{-6}	109
60	1.02×10^{-5}	18.9
65	1.82×10^{-5}	10.6
70	2.83×10^{-5}	6.80

Tabl 6.2b: Rate coefficients for decomposition of the azo group in $FA(EO)_{30}Es$ in water.

Temperature	k_d (s^{-1})	$t_{1/2}$ (h)
50	3.24×10^{-6}	59.4
60	1.02×10^{-5}	18.9
65	1.80×10^{-5}	10.7
70	3.09×10^{-5}	6.23

Table 6.2c: Rate coefficients for decomposition of the azo group in $FA(EO)_{45}Es$ in water.

Temperature	k_d (s^{-1})	$t_{1/2}$ (h)
50	2.20×10^{-6}	87.5
55	3.87×10^{-6}	49.7
60	7.31×10^{-6}	26.4
65	1.93×10^{-5}	9.97
70	3.55×10^{-5}	5.42

Table 6.2d: Rate coefficients for decomposition of the azo group in $FA(EO)_{60}Es$ in water.

Mass (g)	Rate I* (% h^{-1})	Rate II* (% h^{-1})	Polydispersity	Part. size (nm)	Part. number (l^{-1})
3.0	---	---	---	---	-----
3.5	36	18	0.5	164	1.13×10^{17}
4.0	22.5	---	1	167	1.09×10^{17}
4.5	33	22.5	1	146	1.62×10^{17}
5.0	50	22	1	150	1.43×10^{17}
5.5	48	35	1	135	2.01×10^{17}

Table 6.3a: Effect upon the emulsion polymerisation of styrene of varying the mass of $FA(EO)_{24}Es$ at 50°C and with a ratio of styrene to water of 40:100.

*Emulsion polymerisations initiated by $FA(EO)_{24}Es$ and $FA(EO)_{30}Es$ often give conversion-time curves which show two linear portions. The rates corresponding to both portions are cited. The higher rate corresponds to the first part of the curve.

Mass (g)	Rate I* (% h^{-1})	Rate II (% h^{-1})	Polydispersity	Part. size (nm)	Part. number (l^{-1})
3.0	20.5	---	0.5	174	9.60×10^{16}
3.5	---	---	---	---	-----
4.0	32	---	1	135.5	1.97×10^{17}
4.5	60	45	1	113.5	3.32×10^{17}
5.0	60	44	1	121	2.80×10^{17}
5.5	?	63	1	108.5	3.84×10^{17}
6.0	72	---	2	98.5	5.09×10^{17}

Table 6.3b: Effect upon the emulsion polymerisation of styrene of varying the mass of $FA(EO)_{30}Es$ at 50°C and with a ratio of styrene to water of 40:100.

*Refer to Table 6.3a.

Mass (g)	Rate I* (% h^{-1})	Rate II* (% h^{-1})	Polydispersity	Part. size (nm)	Part. number (l^{-1})
3.0	24.7	---	1	141	1.77×10^{17}
3.5	32.5	---	1	133.5	2.10×10^{17}
4.0	38.5	---	1.5	137	1.95×10^{17}
4.5	45	---	1	125.5	2.48×10^{17}
5.0	47.5	---	1	114.5	3.30×10^{17}
5.5	50	---	1.5	114	3.30×10^{17}

Table 6.3c: Effect upon the emulsion polymerisation of styrene of varying the mass of $FA(EO)_{45}Es$ at 50°C and with a ratio of styrene to water of 40:100.

*See Table 6.3a.

Mass (g)	Rate I* (% h^{-1})	Rate II* (% h^{-1})	Polydispersity	Part. size (nm)	Part. number (l^{-1})
3.0	40	---	2	122.5	2.83×10^{17}
3.5	51	---	1	119.5	2.93×10^{17}
4.0	54	---	1.5	113	3.47×10^{17}
4.5	58	---	1	136	1.97×10^{17}
5.0	65	---	1.5	102	4.67×10^{17}
5.5	68.5	---	0.5	105.5	4.18×10^{17}
6.4	79	---	0.5	87	7.55×10^{17}

Table 6.3d: Effect upon the emulsion polymerisation of styrene of varying the mass of $FA(EO)_{60}Es$ at 50°C and with a ratio of styrene to water of 40:100.

*See Table 6.3a.

Temp. (°C)	Rate I* (% h^{-1})	Rate II* (% h^{-1})	Polydispersity	Part. size (nm)	Part. number (l^{-1})
40	14	---	1	168	1.09×10^{17}
45	16.5	---	1	185.5	8.00×10^{16}
50	11	7	0.5	201	6.29×10^{16}
55	8	?	0.5	220	4.70×10^{16}
60	7	27.5	1	216	4.87×10^{16}
65	5	32.5	3	287	2.08×10^{16}

Table 6.4a: Effect upon the emulsion polymerisation of styrene of varying the temperature when the amount of $FA(EO)_{24}Es$ is 1.1×10^{-3} mol and the ratio of styrene to water is 40:100.

*See Table 6.3a.

Temp. (°C)	Rate I* (% h^{-1})	Rate II* (% h^{-1})	Polydispersity	Part. size (nm)	Part. Number (l^{-1})
40	21.4	---	1	132.5	2.17×10^{17}
45	22.7	---	1.5	156	1.33×10^{17}
50	35	25	0	140	1.82×10^{17}
55	12	37.5	0.5	166.5	1.06×10^{17}
60	6.5	36	1	180.5	8.35×10^{16}
65	4	43	2	216.5	4.84×10^{16}

Table 6.4b: Effect upon the emulsion polymerisation of styrene of varying the temperature when the amount of $FA(EO)_{30}$ is 1.1×10^{-3} mol and the ratio of styrene to water is 40:100.

*See Table 6.3a.

Temp. (°C)	Rate I* (% h^{-1})	Rate II* (% h^{-1})	Polydispersity	Part. size (nm)	Part. number (l^{-1})
40	27	---	1.5	127.5	2.39×10^{17}
45	39	---	0.5	121.5	2.76×10^{17}
50	47.5	---	1	114.5	3.30×10^{17}
55	60	---	1	96.5	5.57×10^{17}
60	89	---	2	121	2.74×10^{17}
65	73.5	---	0.5	125.5	2.16×10^{17}

Table 6.4c: Effect upon the emulsion polymerisation of styrene of varying the temperature when the amount of $FA(EO)_{45}Es$ is 1.1×10^{-3} mol and the ratio of styrene to water is 40:100.

*See Table 6.3a.

Temp. (°C)	Rate I* (% h^{-1})	Rate II* (% h^{-1})	Polydispersity	Part. size (nm)	Part. number (l^{-1})
40	36	---	1	111.5	3.65×10^{17}
45	58	---	0	103	4.63×10^{17}
50	79	---	0.5	87	7.53×10^{17}
55	112	---	1	90.5	6.69×10^{17}
60	135	---	1.5	99	5.11×10^{17}

Table 6.4d: Effect upon the emulsion polymerisation of styrene of varying the temperature when the amount of $FA(EO)_{60}Es$ is 1.1×10^{-3} mol and the ratio of styrene to water is 40:100.

*See Table 6.3a.

Weight (g)	Rate I* (% h^{-1})	Rate II* (% h^{-1})	Polydispersity	Part. size (nm)	Part. number (l^{-1})
4.0	19.3	---	1	168	1.08×10^{17}
5.0	25.4	---	1.5	128	2.36×10^{17}
6.0	35.0	---	2	122	2.70×10^{17}
7.0	43.3	---	2	108.5	3.81×10^{17}

Table 6.5a: Effect upon the emulsion polymerisation of styrene of varying the amount of $FA(EO)_{24}Es$ at 45°C and with a ratio of styrene to water of 40:100.

Weight (g)	Rate I* (% h^{-1})	Rate II* (% h^{-1})	Polydispersity	Part. size (nm)	Part. number (l^{-1})
3.0	10	---	0.5	184	8.37×10^{16}
4.5	41	---	2	115	3.14×10^{17}
5.5	54	---	2	107	4.01×10^{17}
6.5	73	---	2	105	4.20×10^{17}

Table 6.5b: Effect upon the emulsion polymerisation of styrene of varying the amount of $FA(EO)_{30}Es$ at 45°C and with a ratio of styrene to water of 40:100.

*See Table 6.3a.

Temp. (°C)	Rate I* (% h^{-1})	Rate II* (% h^{-1})	Polydispersity	Part. size (nm)	Part. number (l^{-1})
35	13	10	1	144.5	1.28×10^{17}
45	29	---	0.5	168	7.98×10^{16}
50	32	17.5	0.5	154	1.05×10^{17}
55	41	18	1	175	7.06×10^{16}
65	24	6.2	1.5	230	3.02×10^{16}

Table 6.6: Effect upon the emulsion polymerisation of styrene of varying the temperature when the amount of $FA(EO)_{24}Es$ is 1.1×10^{-3} mol and the ratio of styrene to water is 40:145.

*See Table 6.3a.

Vol. water (ml)	Rate I* (% h^{-1})	Rate II* (% h^{-1})	Polydispersity	Part. size (nm)	Part. number (l^{-1})
72	---	---	2	202.5	7.39×10^{16}
100	16.5	---	1	185.5	8.00×10^{16}
145	24	---	0.5	168	7.98×10^{16}
181	36	---	0.5	156	8.38×10^{16}

Table 6.7a: Effect upon the emulsion polymerisation of 40 ml of styrene of varying the volume of water at 45°C when the amount of $FA(EO)_{24}Es$ is 1.1×10^{-3} mol.

Vol. water (ml)	Rate I* (% h^{-1})	Rate II* (% h^{-1})	Polydispersity	Part. size (nm)	Part. number (l^{-1})
72	21.4	---	1.5	151	1.81×10^{17}
100	22.7	---	1.5	156	1.33×10^{17}
145	29.5	---	1	178.5	6.78×10^{16}
181	33	---	2	157	8.14×10^{16}

Table 6.7b: Effect upon the emulsion polymerisation of 40 ml of styrene of varying the volume of water at 45°C when the amount of $FA(EO)_{30}Es$ is 1.1×10^{-3} mol.

*See Table 6.3a.

Vol. water (ml)	Rate I* (% h^{-1})	Rate II* (% h^{-1})	Polydispersity	Part. size (nm)	Part. number (l^{-1})
72	41	---	2	124.5	3.23×10^{17}
100	39	---	0.5	121.5	2.76×10^{17}
145	43	---	1	109	2.89×10^{17}
181	44	---	2	110	3.32×10^{17}

Table 6.7c: Effect upon the emulsion polymerisation of 40 ml of styrene of varying the volume of water at 45°C when the amount of $FA(EO)_{45}Es$ is 1.1×10^{-3} mol.

Vol. water (ml)	Rate I* (% h^{-1})	Rate II* (% h^{-1})	Polydispersity	Part. size (nm)	Part. number (l^{-1})
72	55	---	1	106	5.19×10^{17}
100	58	---	0	103	4.63×10^{17}
145	60	---	1.5	108.5	2.88×10^{17}
181	56	---	1	103	2.80×10^{17}

Table 6.7d: Effect upon the emulsion polymerisation of 40 ml of styrene of varying the volume of water at 45°C when the amount of $FA(EO)_{60}Es$ is 1.1×10^{-3} mol.

*See Table 6.3a.

Measurements carried out using an electron microscope				Measurements carried out using a Coulter Nanosizer			
Rxn t (min)	d_v (nm)	Polydispersity	Part. no. (l^{-1})	Polydispersity	d_v (nm)	Surf. tens. (dyne/cm)	% Conversion
40	117.4	1.038	8.52×10^{16}	1	141	39	21
60	139.8	1.010	5.81×10^{16}	1	160.5	38.5	25
120	152.0	1.017	6.12×10^{16}	1	169.5	38.5	37
170	168.4	1.016	5.35×10^{16}	0.5	175	40	46
220	195.0	1.013	3.96×10^{16}	1	179.5	39	54
240	186.2	1.007	4.80×10^{16}	1	192	39.5	57
260	188.9	1.015	4.84×10^{16}	1	203	39.5	61
270	190.2	1.012	4.89×10^{16}	0.5	190	40.5	63
280	194.1	1.009	4.70×10^{16}	0	209	41.5	64
290	204.9	1.015	4.12×10^{16}	0	215.5	39	67
300	195.0	1.012	4.95×10^{16}	0	200	40.5	69
320	208.7	1.014	4.46×10^{16}	0	198	42	77
330	116.3	1.786	3.05×10^{17}	0	202	41	93

Table 6.8: Results for particle sizes, particle numbers and surface tension for latices produced by FA$(EO)_{24}$Es at 60°C.

Measurements carried out using an electron microscope				Measurements carried out using a Coulter Nanosizer			
Rxn t (min)	d_v (nm)	Polydispersity	Part. no. (l^{-1})	Polydispersity	d_v (nm)	Surf. tens. (dyne/cm)	% Conversion
15	53.6	1.041	5.47×10^{17}	1.5	62.5	40	8
30	92.0	1.030	1.58×10^{17}	1.5	99.5	40	16
45	118.4	1.036	8.88×10^{16}	0.5	118	40	21
75	126.4	1.037	9.12×10^{16}	1	146.5	40.5	29
120	148.0	1.020	7.24×10^{16}	0.5	151.5	40.75	40
150	155.4	1.019	7.08×10^{16}	0	171	42.25	46
180	173.4	1.015	5.66×10^{16}	1	178	42.75	53
200	176.1	1.009	5.88×10^{16}	0.5	172.5	43.25	58
240	144.8	1.370	1.38×10^{17}	2.5	172.5	45.25	66
255	100.4	1.798	4.65×10^{17}	0	190.5	47.5	79

Table 6.9: Results for particle sizes, particle numbers and surface tension for latices produced by FA$(EO)_{30}$Es at 60°C.

Measurements carried out using an electron microscope				Measurements carried out using a Coulter Nanosizer			
Rxn t (min)	d_v (nm)	Polydispersity	Part. no. (l^{-1})	Polydispersity	d_v (nm)	Surf. tens. (dyne/cm)	% Conversion
15	51.4	1.187	4.54×10^{17}	3	75.5	41.5	3
30	60.2	1.090	3.88×10^{17}	2.5	68.5	40.75	8
50	59.9	1.111	5.49×10^{17}	1.5	79	41	15
80	77.8	1.092	3.64×10^{17}	1	95.5	41.5	26
110	94.4	1.040	2.65×10^{17}	2	128	41	37
140	98.8	1.167	2.73×10^{17}	2.5	132.5	41	46
170	112.5	1.029	2.13×10^{17}	2.5	132	41.75	55
200	111.5	1.022	2.44×10^{17}	3	150.5	43	62
245	116.8	1.134	2.50×10^{17}	2.5	135.5	45	75
290	117.9	1.030	2.81×10^{17}	1	149.5	46	88

Table 6.10: Results for particle sizes, particle numbers and surface tension for latices produced by FA $(EO)_{30}Es$ at 40°C.

Measurements carried out using an electron microscope				Measurements carried out using a Coulter Nanosizer			
Rxn t (min)	d_v (nm)	Polydispersity	Part. no. (l^{-1})	Polydispersity	d_v (nm)	Surf. tens. (dyne/cm)	% Conversion
10	58.3	1.134	5.15×10^{17}	3.5	60	44.75	4
15	66.8	1.077	4.19×10^{17}	3	64.5	44.25	9
20	74.1	1.066	4.00×10^{17}	3	74	43.75	18
25	77.3	1.063	4.44×10^{17}	2	79.5	44.5	27
30	82.2	1.043	4.53×10^{17}	1	91	45.75	37
35	83.1	1.082	5.21×10^{17}	1	82	46.25	47
40	90.7	1.070	4.61×10^{17}	1	94	46.25	57
45	109.2	1.015	3.10×10^{17}	0.5	96	44.5	70
50	106.6	1.018	3.70×10^{17}	1	94.5	47	80

Table 6.11: Results for particle sizes, particle numbers and surface tension for latices produced by FA$(EO)_{60}$Es at 60°C.

Measurements carried out using an electron microscope				Measurements carried out using a Coulter Nanosizer			
Rxn t (min)	d_v (nm)	Polydispersity	Part. no. (l^{-1})	Polydispersity	d_v (nm)	Surf. tens. (dyne/cm)	% Conversion
30	60.9	1.159	4.56×10^{17}	5	62.5	44.5	5
50	53.6	1.190	7.67×10^{17}	2	70	44.25	8
70	82.0	1.081	2.60×10^{17}	2	90	44.5	13
90	71.7	1.132	4.83×10^{17}	1.5	88.5	44.5	21
110	73.5	1.203	5.62×10^{17}	1	103	45.25	31
130	79.7	1.036	5.45×10^{17}	1	98	46.25	42
150	90.0	1.031	4.25×10^{17}	1	103	46.75	54
170	77.0	1.109	7.76×10^{17}	1	100	47	59
190	93.2	1.101	4.62×10^{17}	1	107.5	48.5	64

Table 6.12: Results of particle sizes, particle numbers and surface tension for latices produced by $FA(EO)_{60}$ at 40 °C.

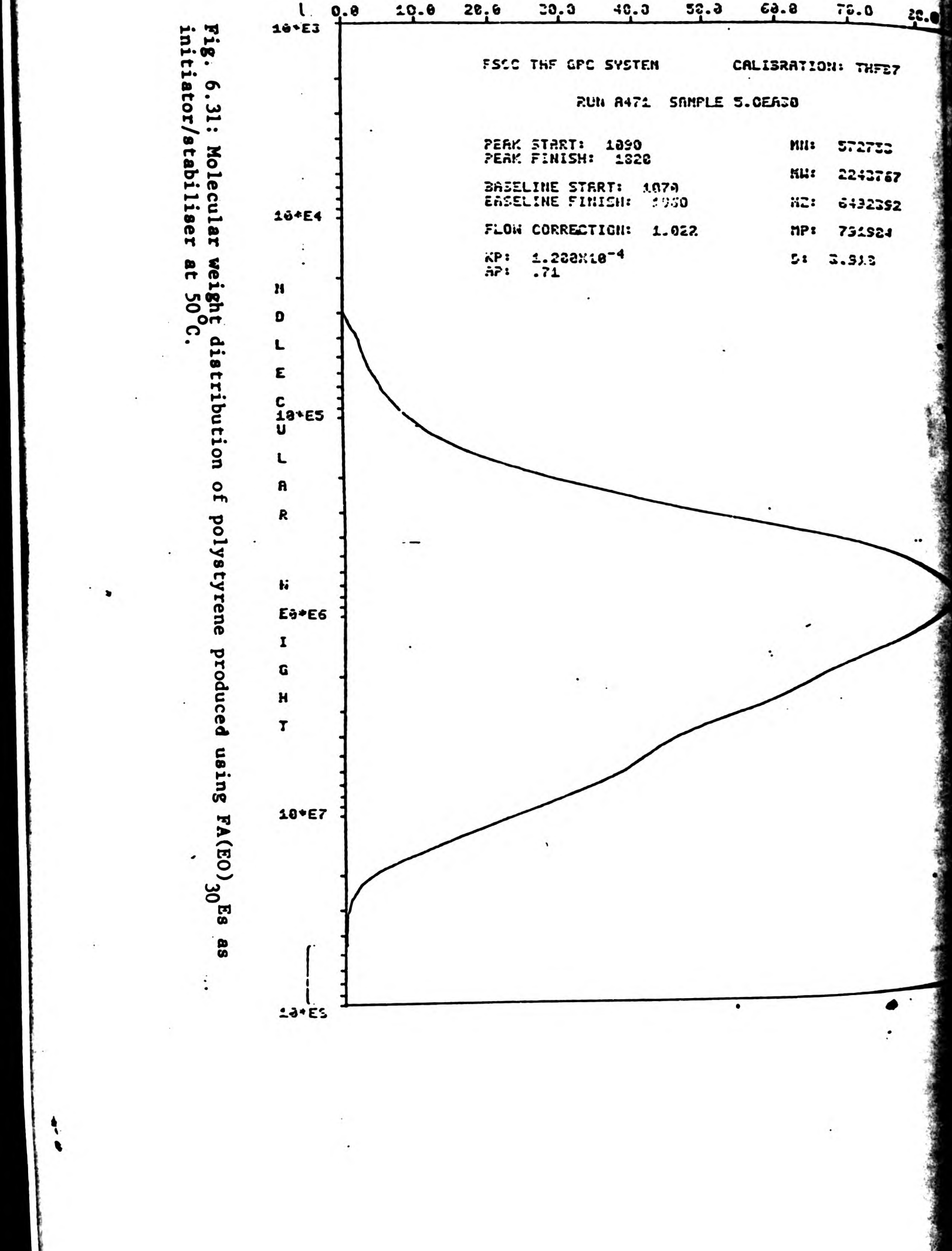


Fig. 6.31: Molecular weight distribution of polystyrene produced using FA(EO)$_{30}$Es as initiator/stabiliser at 50^{o}C.

Mass of initiator (g)	M_n	M_w	D
3.0	-----	-----	---
4.0	610 000	2 700 000	4.5
4.5	513 000	2 270 000	4.4
5.0	970 000	2 810 000	2.3
5.5	442 000	2 000 000	4.6

Table 6.13a: Variation in the molecular weight of polystyrenes prepared with variable concentration of $FA(EO)_{24}Es$ at 50°C.

Mass of initiator (g)	M_n	M_w	D
3.0	675 000	2 300 000	3.4
3.6	-----	-----	---
4.5	1 170 000	3 400 000	2.9
5.0	572 000	2 243 000	3.9
5.5	486 000	2 333 000	4.8

Table 6.13b: Variation in the molecular weight of polystyrenes prepared with variable concentration of $FA(EO)_{30}Es$ at 50°C.

Mass of initiator (g)	M_n	M_w	D
3.0	790 000	2 480 000	3.1
4.0	750 000	2 361 000	3.1
5.0	-----	-----	---
5.5	628 000	2 573 000	4.1

Table 6.13c: Variation in the molecular weight of polystyrenes prepared with variable concentration of $FA(EO)_{45}Es$ at 50°C.

Mass of initiator (g)	M_n	M_w	D
3.0	414 000	1 934 000	4.7
4.0	715 000	2 426 000	3.4
5.0	287 000	1 300 000	4.5
5.5	382 000	2 000 000	5.2
6.4	-----	-----	---

Table 6.13d: Variation in the molecular weight of polystyrenes prepared with variable concentration of $FA(EO)_{60}Es$.

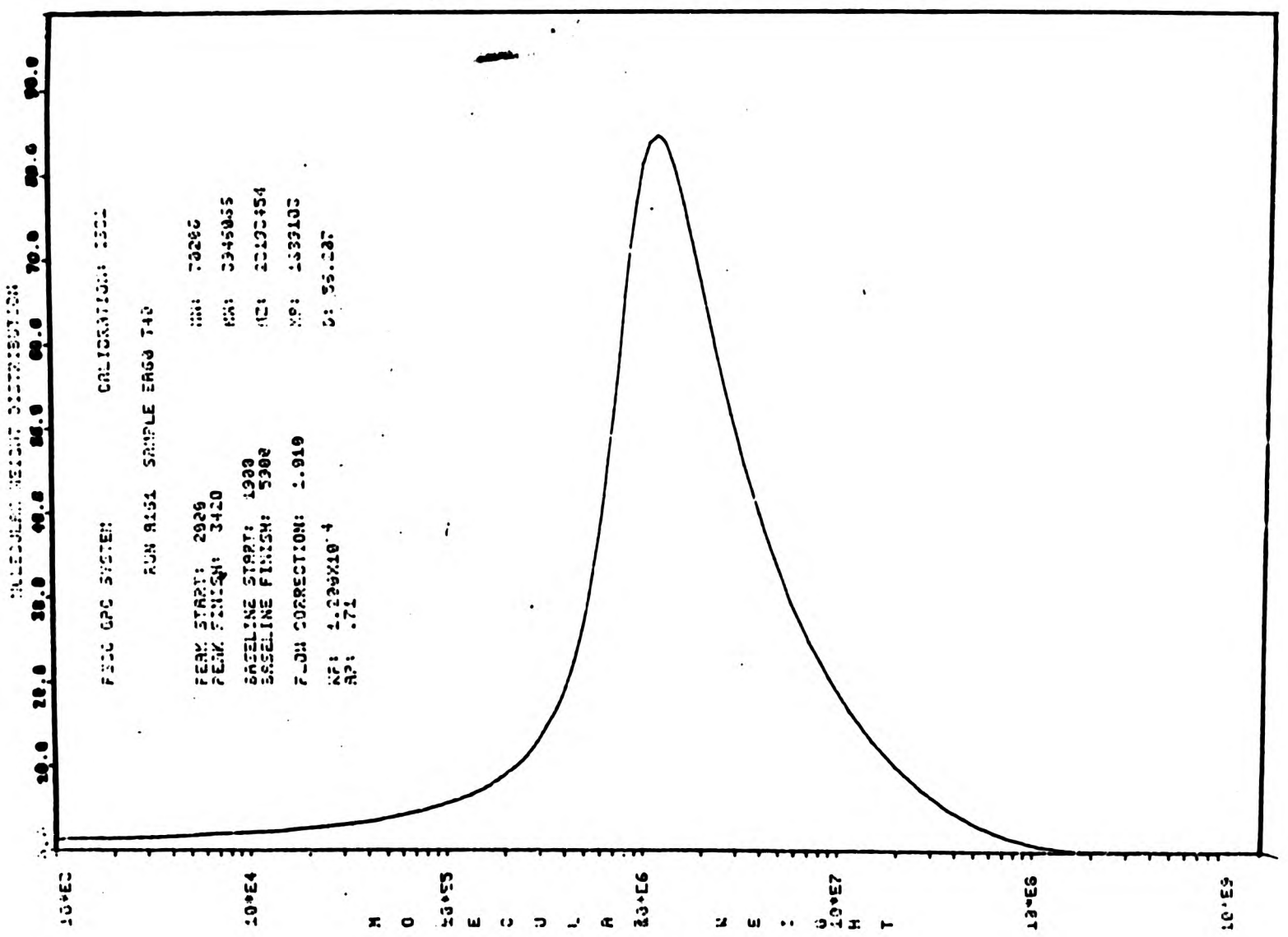


Fig. 6.33: Molecular weight distribution of polystyrene produced using 1.1×10^{-3} mol of $FA(EO)_{60}Es$ as initiator/stabiliser at 40°C.

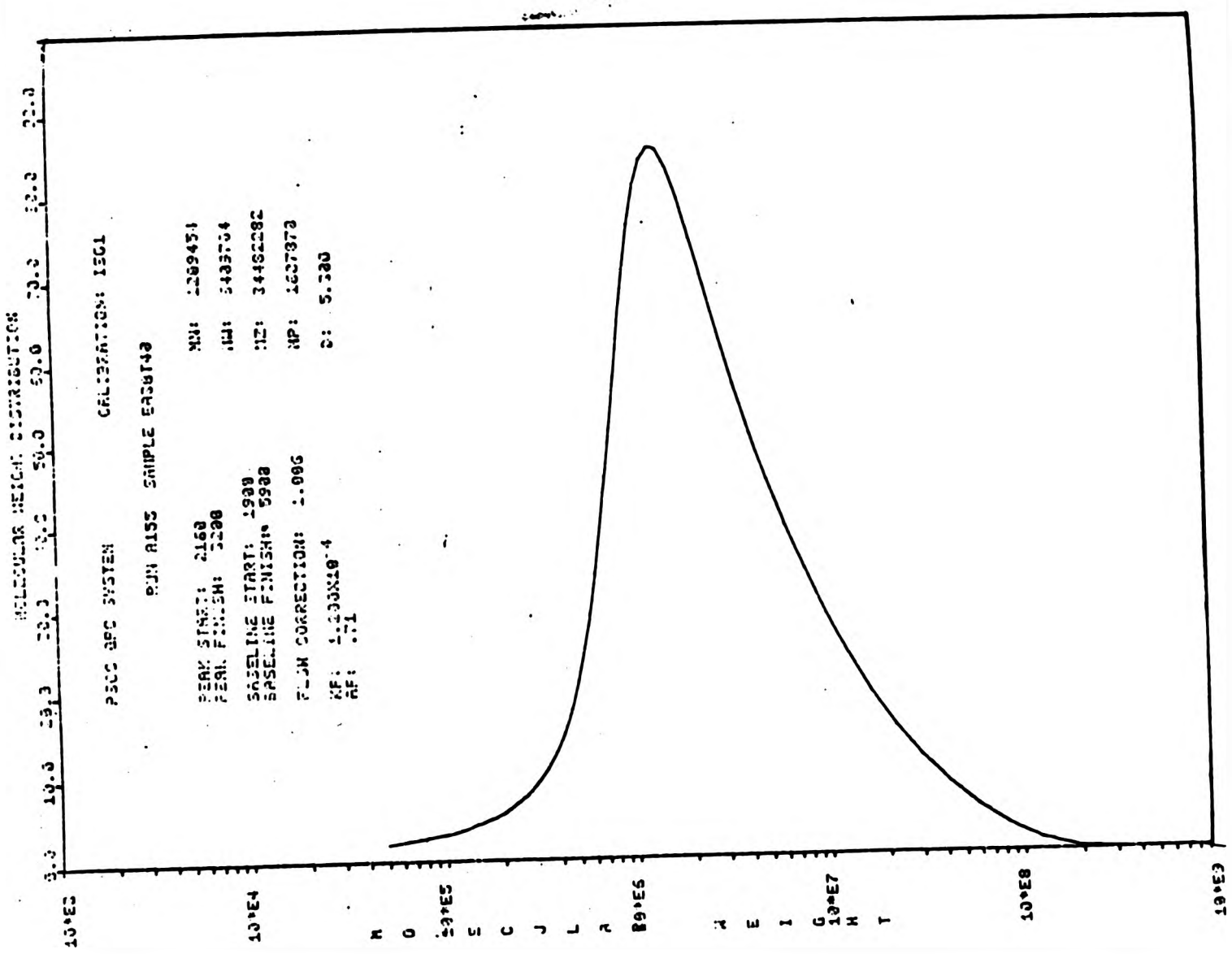


Fig. 6.34: Molecular weight distribution of polystyrene produced using 1.1×10^{-3} mol of $FA(EO)_{30}Es$ as initiator/stabiliser at 40°C.

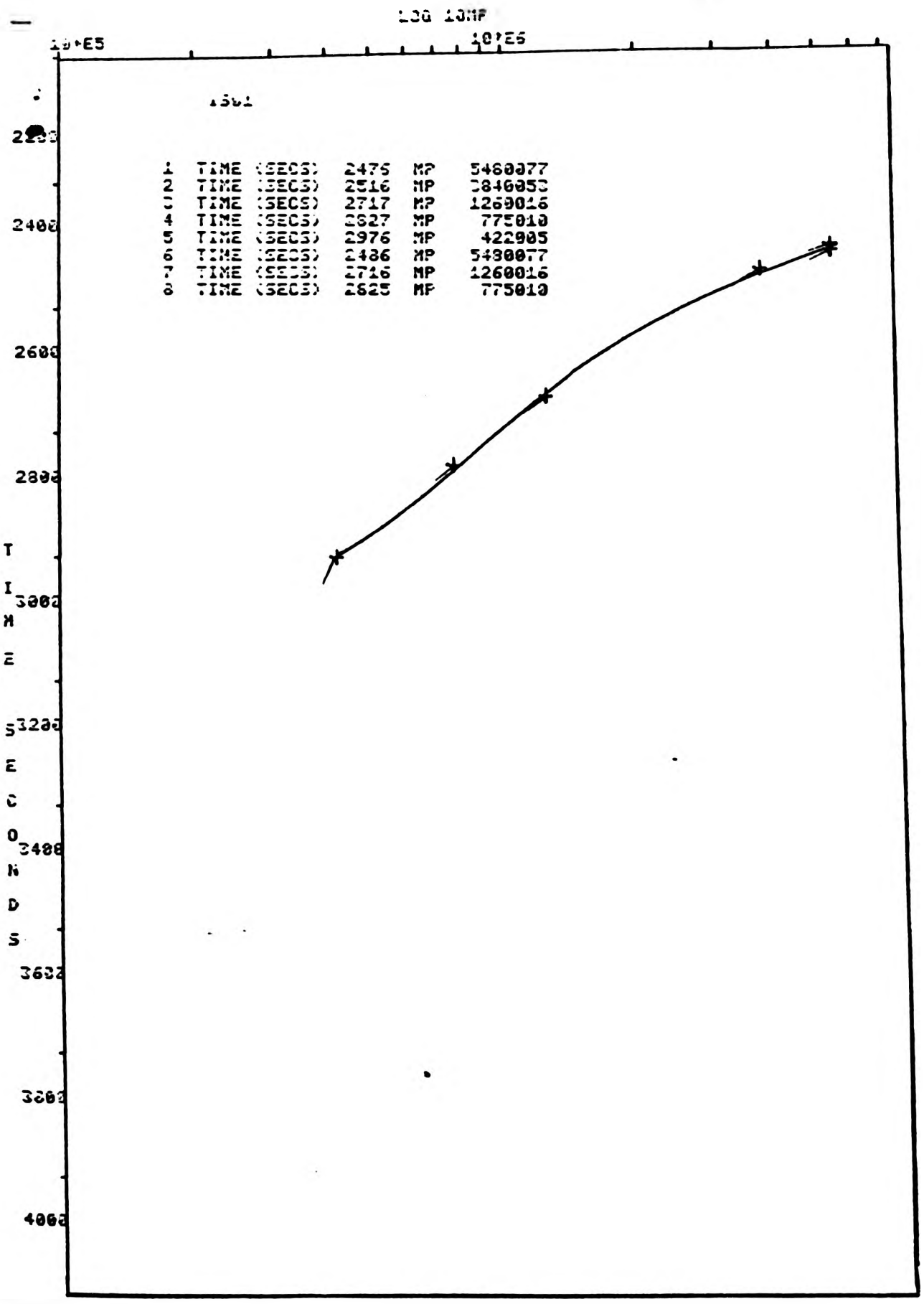


Fig. 6.35: Molecular weight calibration.

Initiator	Molecular weight (GPC) M_n	M_w	D	MW (LALLS) M_w
$FA(EO)_{24}Es$	2 300 000	10 000 000	4.4	7 000 000
$FA(EO)_{30}Es$	1 200 000	5 400 000	5.3	5 500 000
$FA(EO)_{45}Es$	630 000	4 400 000	6.9	3 750 000
$FA(EO)_{60}Es$	70 200	4 000 000	5.6	3 700 000

Table 6.14a: Molecular weights of polystyrenes produced at 40°C determined by high-molecular-weight calibrations and by low-angle laser light scattering.

Initiator	Molecular weight (GPC) M_n	M_w	D
$FA(EO)_{24}Es$	996 000	5 000 000	5.1
$FA(EO)_{30}Es$	2 300 000	13 700 000	5.9
$FA(EO)_{45}Es$	1 700 000	12 000 000	7.0
$FA(EO)_{60}Es$	1 800 000	16 500 000	9.1

Table 6.14b: Molecular weights of polystyrenes produced at 50°C determined by high-molecular-weight calibrations.

Initiator	Molecular weight (GPC) M_n	M_w	D
$FA(EO)_{24}Es$	12 000	1 200 000	?
$FA(EO)_{30}Es$	363	1 500 000	?
$FA(EO)_{45}Es$	1 000 000	3 100 000	3.0
$FA(EO)_{60}Es$	260 000	4 400 000	16.4?

Table 6.14c: Molecular weights of polystyrenes produced at 60°C determined by high-molecular-weight calibrations.

Initiator	1.1×10^{-3} mol initiator:	Yield of polymer from 40 ml styrene (g)	% Yield	% Yield (h^{-1})	Time of reaction (h)
AZBN	0.174	3.8	10.0	1.7	6
$FA(EO)_{14}Es$	0.53	3.4	9.4	1.6	6
$FA(EO)_{24}Es$	0.76	3.0	8.3	1.4	6
$FA(EO)_{30}Es$	0.90	3.2	8.9	1.5	6
$FA(EO)_{45}Es$	1.25	3.2	8.9	1.5	6
$FA(EO)_{60}Es$	1.60	3.4	9.4	1.6	6

Table 6.15: Results for bulk polymerisation of styrene at 50°C.

CHAPTER SEVEN

DISCUSSION OF RESULTS AND CONCLUSIONS

7.1. Discussion of results.

7.1.1. Introduction. Conventional emulsion polymerisation systems, in which an ionic salt and a water-soluble initiator are used, have been extensively studied[23,180,34,181]. Also, emulsion polymerisation reactions using non-ionic surfactants and oil-soluble initiators have been carried out[182,185]. A mixture of an ionic and a non-ionic emulsifier with an ionic initiator has also been used[184,183,186]. It appears that, in general, when water-insoluble monomers are used, the course of the reaction is divided into three well-defined stages. First there is a period, typically lasting up to 10% conversion, during which the rate of polymerisation increases from zero. Then there is a period of constant rate, during which the number of growing polymer particles is constant. Finally there is a period in which the rate decreases. These three stages yield the well-known S-shaped curves for plots of conversion versus time. However, quite a few results have been obtained which indicate that the number of particles can change during the second stage of an emulsion polymerisation reaction, e.g., those of Robb[78], particularly when water-soluble monomers are used.

Smith and Ewart derived the following mathematical relationship for the rate of polymerisation during Interval II for emulsion polymerisation reactions which conform to certain limiting conditions:

$$R_p = \tfrac{1}{2} k_p N [M] \qquad (2.5)$$

This equation predicts that the rate of polymerisation during Interval II for a given number of particles is independent of the initiator concentration. In deriving the above equation, it has been assumed (among other things) that the primary radicals enter the particles one by one. This assumption is fulfilled for water-soluble initiators, and probably for oil-soluble initiators activated by water-soluble compounds, e.g., some redox systems. Van der Hoff[51] claims that, if an activated oil-soluble

initiator is employed which decomposes into radical pairs within the particles, the assumption that primary radicals enter the particle one by one does not hold.

Smith and Ewart maintain that the initiator concentration during Interval II has no measurable effect on the initial rate of polymerisation in polystyrene seed particles. The tendency towards increased rate with increased conversion in seeded polymerisations in the case of high concentrations of persulphate initiator is explained as probably due to the formation of new particles.

Increasing the rate of generation of free radicals in the aqueous phase without changing the number of particles will decrease the interval between successive entrances of free radicals into a particle. This will not affect the rate of polymerisation, but it will decrease the degree of polymerisation.

Another assumption of the theory is that, while there are monomer droplets present, the monomer concentration in the monomer-polymer particles is constant. However, this does not seem to be always the case[79].

According to the theory, the rate of polymerisation is directly proportional to the number of polymer particles formed in Interval I. As was shown in Chapter Two, Smith and Ewart derived the following relationship in which the number of polymer particles formed in Interval I is related to the surfactant concentration and to the rate of generation of free radicals in the aqueous phase:

$$N = k\,(\rho/\mu)^{2/5}\,(a_s S)^{3/5} \qquad (2.8)$$

Thus the number of particles, N, is predicted to be proportional to the number of growing radicals to the 2/5 power and to the concentration of micellar emulsifier to the 3/5 power.

The theoretical predictions contained in the above equation have been tested by a number of authors, most extensively by Bartholome et al[187].

It has been found that the number of particles formed is accurately proportional to the 2/5 power of the concentration of initiator. A number of experimental studies confirm that the number of particles is proportional to the 3/5 power of the concentration of soap[188,25]. S refers to the concentration of micellar soap, thus, when using a fixed concentration of soaps of different cmc's, it has been observed that the number of particles, and therefore the rate of polymerisation, decreases sharply with increasing cmc[189].

Van der Hoff[51] has attempted to verify the Smith-Ewart theory with respect to the absolute number of particles formed. His findings show fair agreement with the equation. However, particle formation also occurs when the soap concentration is lower than the cmc[189], and indeed when no surfactant is present at all[14]. When micellar nucleation of latex particles is predominant, Dunn et al[190] report that there is evidence to show that the size of the initial micelle is an important factor in the emulsion polymerisation of styrene.

During Interval I, an increase in initiator concentration, surfactant concentration[79] or temperature will result in an increase in the number of particles and therefore in an increase in the rate of polymerisation during both Interval I and Interval II. However, once Interval II is reached, the theory predicts that the number of particles remains constant and the only way of increasing the rate of polymerisation is by increasing the temperature.

Constancy of N has indeed been demonstrated in many cases. For example, in the polymerisation of styrene initiated by the oil-soluble azobisisobutyronitrile, N remains constant throughout Interval II[191]. Nevertheless, besides data consistent with the ideas of Smith and Ewart, quite a few results are known which indicate that a change in the number of particles can occur during the second stage of emulsion polymerisation reactions. Thus Robb[78] has shown that the number of latex particles is not constant during Interval II of the emulsion polymerisation of styrene, but increases by about 50%. Since a constant rate is observed, this can only be explained by a falling monomer concentration within the growing particles, compensating for the effect of increasing particle numbers[78].

7.1.2. Initiation of emulsion polymerisation when oil-soluble initiators are used. Some oil-soluble initiators, e.g., benzoyl peroxide, although good initiators for solution polymerisation, are poor initiators for emulsion polymerisation reactions. Other thermally decomposable peroxides and azo compounds produce polymer in emulsion systems at rates comparable to those observed in polymerisations initiated by water-soluble initiators, where the radicals enter the particles one by one. It seems that, although oil-soluble initiators presumably decompose into radical pairs within the particles, polymer radicals are formed one by one. One possible way in which this can occur is the entry of single radicals from the aqueous phase. The rate of entry of such radicals should depend upon the concentration of the initiator in the water. This concentration is not so much determined by the solubility of the catalyst in water as by its partition coefficient between the organic and the aqueous phases. Another mechanism is rapid exit of one of the pair of radicals from a micelle or particle.

Lim[192] found that the decomposition of azo compounds is a unique type of reaction, in which the strongly endothermic formation of radicals by cleavage of the single bonds is facilitated by the exothermic release of nitrogen. If no concurrent reaction occurs, the decomposition of azo compounds is a strictly first-order reaction whose rate depends mainly on the substituent groups in the compound and relatively little on the medium in which the azo compound is dissolved.

A wide variety of substituents can be incorporated into the azo initiator. This variability can be used to good effect in tailoring the properties of the initiator to meet more closely the requirements of the polymerisation system[193]. Azo initiators offer great possibilities to the emulsion polymer manufacturer. Decomposition rates and molecular structure can be modified to meet specific requirements and the use of different substituent groups within the initiator may enable improved addition, coalescence, etc., to be conferred on the polymer via incorporation of these substituents as end-groups.

Dunn and coworkers[194] have studied the efficiency of azobisisobutyronitrile in the emulsion polymerisation of styrene. Like Van

der Hoff, these workers claim that the isolation of a polymer radical in the latex particle is dependent on the probablity of one radical escaping into the aqueous phase by partition or by transfer to an emulsifier molecule.

In emulsion polymerisation, when an oil-soluble initiator is used, the initiator radical must escape entirely from the micelle or latex particle in which it was produced. Thus a lower efficiency of initiation may be expected than from water-soluble initiators.

Dunn et al[194] maintain that the number of latex particles formed varies approximately as the 2/5 power of the initiator concentration, but the dependence of the rate of polymerisation during Interval II on the initiator concentration is lower than this, indicating that the dependence of the rate during Interval II is such that the rate is less than directly proportional to the number of latex particles present, as required by the Smith-Ewart theory. This result is similar to that found when using more water-soluble monomers in which the transfer of radicals from the particles to the aqueous phase is not negligible. Studies on the diffusion of reactive radicals have been carried out by Smith[148].

Dunn et al[194] suggest that the dependence of the rate during Interval II is such that a rate less than directly proportional to the number of latex particles present might be expected, since the possibility of using an oil-soluble initiator for an emulsion polymerisation depends on the transfer of radicals to the aqueous phase. The number of latex particles formed using a high concentration of azobisisobutyronitrile was the same as that using a much lower concentration of potassium persulphate. It seems that only some 4% of the radicals available for the initiation of polymerisation in the oil phase actually nucleate latex particles. The remainder probably initiate polymerisation in the oil phase. However, because of the small volume of the latex particle, the radical concentration must be very high and thus mutual termination of radicals is rapid. Thus only a small amount of oligomer is formed, which is probably left behind in solution on precipitation and isolation of the polymer produced.

Tentatively put forward in the same paper is the suggestion that the

probability of transfer to the emulsifier increases with the length of the alkyl chain of the emulsifier. Increasing probability of transfer implies increasing probability of radicals escaping into the aqueous phase. The authors conclude that when azobisisobutyronitrile is used as an initiator for the emulsion polymerisation of styrene, case I kinetics should apply.

7.2. Relevance to present work: summary of results. The work carried out during this investigation has involved the emulsion polymerisation of styrene in the presence of compounds that acted simultaneously as initiators for polymerisation as well as stabilisers for the final latex formed. These compounds were esters of 4,4'-azobis-4-cyanopentanoic acid and various fatty-alcohol ethoxylates synthesised during this investigation. These esters are soluble in the monomer as well as in the dispersion medium. Direct measurements of the solubility of these compounds proved impossible to carry out because these esters are very soluble in both oil and water phases. Measurements of the partition of these compounds between the oil and the water phases are complicated by the dual nature of the ester molecules; i.e., these compounds contain a hydrophilic end as well as a hydrophobic portion, making separation of the oil and the water phases very difficult. Thus, any conclusions as to the relative solubility of these initiator/stabilisers will have to be drawn from the results obtained whilst studying the effects that different variables have on the emulsion polymerisation of styrene.

Also, the esters, as well as the fatty-alcohol ethoxylates themselves, show the inverse solubility phenomenon; i.e., each compound has a certain temperature at and above which it is less soluble than at room temperature. Table 6.1 in Chapter Six gives information on the solubilities of the esters in water at different temperatures. Thus, for example, $FA(EO)_{24}Es$ is soluble at room temperature but only partially soluble at 70°C. If the solution is cooled down, the ester redissolves in the water. At 75°C, $FA(EO)_{24}Es$ becomes insoluble; i.e., more ester precipitates than at 70°C. $FA(EO)_{45}Es$ and $FA(EO)_{60}Es$ do not show direct signs of inverse solubility in the range of temperatures studied. From these observations, approximate cloud points were estimated. The half-lives for the thermal decomposition of the esters are given in Table 6.2. It has been concluded that the insolubility of the esters at high

temperatures is caused by a physical effect such as an increase in the thermal motion of the molecules breaking the hydrogen bonds that confer the water-solubility, rather than the production of insoluble products by rapid thermal decomposition. All the polymerisations have been conducted at temperatures below the estimated cloud point of the ester in water.

The solubilities of the fatty-alcohol ethoxylates in water, as well as those of the esters derived from them, are presumably a consequence of the polyoxyethylene chain present in the hydrophilic portion of the fatty-alchol ethoxylates. This water-solubility is caused by the formation of a number of hydrogen bonds between the water and the polyoxyethylene chains. As the temperature increases, and as a result of increased kinetic energy, some of the hydrogen bonds break. When a temperature is reached at which the number of hydrogen bonds broken is sufficiently high, the compound becomes insoluble.

The hydrophilic/lipophilic balances for the fatty-alcohol ethoxylates have been reported by Blackley et al[195]. Values range from 14.4 for $FA(EO)_{14}H$ to 18.3 for $FA(EO)_{60}H$. The HLB value for the esters is expected to be lower, since the CH_2 content of the ester is greater. These workers also give calculated distributions of the chain length of the ethylene oxide units. Thus $FA(EO)_{60}H$, for instance, is predicted to comprise mainly a mixture of molecules which contain from 40 to 70 ethylene oxide units.

In the present investigation, the first result obtained was the conversion versus time curves for the emulsion polymerisation of styrene at 50°C. When the molar concentration of initiator was kept constant at 1.1×10^{-3} mol per 40 ml of styrene. The initiators studied were $FA(EO)_{24}Es$, $FA(EO)_{30}Es$, $FA(EO)_{45}Es$ and $FA(EO)_{60}Es$. Also, the conversion versus time curves of the emulsion polymerisation of styrene at 50°C were obtained when constant weights (5.0 g per 40 ml of styrene) of $FA(EO)_{14}Es$, $FA(EO)_{24}Es$, $FA(EO)_{30}Es$, $FA(EO)_{45}Es$ and $FA(EO)_{60}Es$ were used as initiator/stabilisers for the emulsion polymerisation of styrene. Because of the low rate of polymerisation given by $FA(EO)_{14}Es$, it was discarded from the in-depth study. These results are given in Figs.

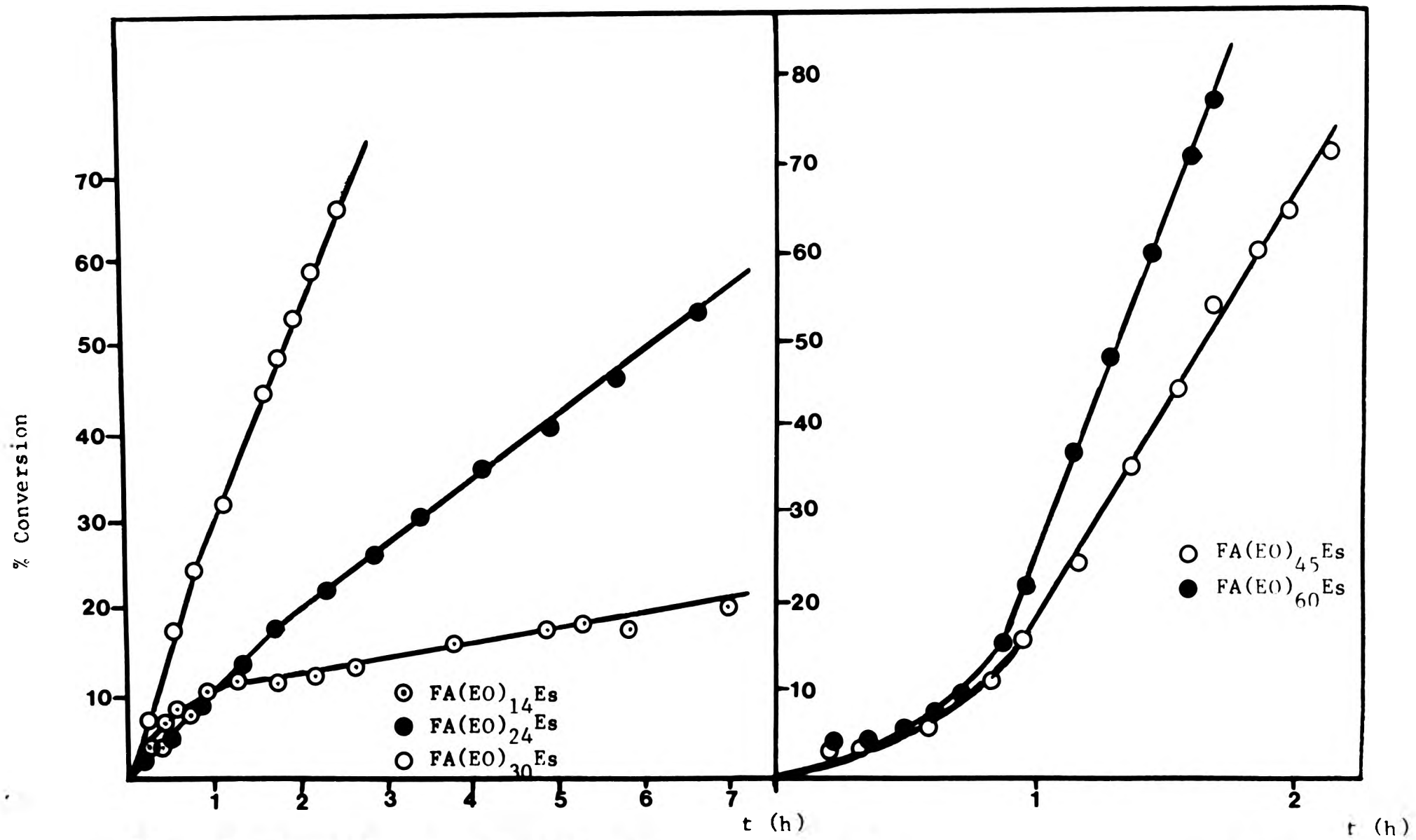


Fig. 7.1a: Conversion-time curves for the emulsion polymerisation of styrene using $FA(EO)_{14}Es$ (5.0 g), $FA(EO)_{24}Es$ and $FA(EO)_{30}Es$ (1.1×10^{-3} mol) as initiator/stabilisers at 50°C

Fig. 7.1b: Conversion-time curves for the emulsion polymerisation of styrene using $FA(EO)_{45}Es$ and $FA(EO)_{60}Es$ (1.1×10^{-3} mol) at 50°C.

6.1 and 6.2. Some of these results are re-presented in Fig. 7.1, from which it appears that the curves obtained can be divided into three groups: (i) that given by $FA(EO)_{14}Es$; (ii) those given by $FA(EO)_{24}Es$ and $FA(EO)_{30}Es$; and (iii) those given by $FA(EO)_{45}Es$ and $FA(EO)_{60}Es$. The last group by and large resemble curves observed for conventional emulsion polymerisation reactions. They differ from the curves for conventional emulsion polymerisation reactions in that the straight-line portion continues up to 80-85% conversion in some cases, instead of tailing off at approximately 60% conversion. An attempt to explain this observation will be made at a later stage. The curves given by $FA(EO)_{24}Es$ and $FA(EO)_{30}Es$ at 50°C, however, do not resemble those observed for conventional emulsion polymerisation reactions. The curve given by $FA(EO)_{14}Es$ bears even less resemblance to the curves given by conventional emulsion polymerisation reactions.

7.2.1. Kinetics of decomposition of the azo group of the initiator in water. The rates of decomposition of the azo groups of the esters in water at different temperatures were studied using ultraviolet spectroscopy. The values obtained for the activation energies of the azo groups were as follows:

Ester	Activation energy (kJ/mol)	A value
$FA(EO)_{24}Es$	164.2	6.04×10^{20}
$FA(EO)_{30}Es$	132.3	4.64×10^{15}
$FA(EO)_{45}Es$	105.8	3.94×10^{11}
$FA(EO)_{60}Es$	135.1	1.33×10^{16}

Table 7.1: Activation energies for the decomposition of the azo group of the initiator/stabiliser in water.

The literature values for the sodium salt of 4,4'-AB-4-CPA are 134.2 kJ/mol[156] and 142.3 kJ/mol[196]. For AZBN, the activation energies show a greater range[196], e.g., 128.4 kJ/mol, 123.4 kJ/mol, 128.9 kJ/mol, 127.6 kJ/mol, 121.2 kJ/mol, 142.3 kJ/mol, 131.0 kJ/mol.

7.2.2 Effect of initiator/stabiliser concentration upon the shapes of the conversion-time curves and upon the rates of polymerisation. When studying the effect of concentration of $FA(EO)_{24}Es$ upon the emulsion polymerisation of styrene at 50°C, it was realised that the shape of the conversion-time curve depended upon the concentration of initiator/stabiliser. At very low concentrations (ca. 3.0 g per 40 ml of styrene), the curve resembles that for a typical bulk polymerisation. At high ester concentrations (ca. 7.0 g per 40 ml of styrene), the curve obtained was similar to that for a typical emulsion polymerisation. At intermediate concentrations, the curves resembled neither that typical of bulk polymerisations nor that typical of conventional emulsion polymerisations (Fig. 6.5). The curves obtained when $FA(EO)_{30}Es$ was the initiator/stabiliser resembled those for reactions initiated by $FA(EO)_{24}Es$, although there is an apparent lack of nucleation period (Fig. 6.6). Although the shape of the emulsion polymerisation curves appears to depend upon the initiator concentration, it is observed that, as expected, the rate of polymerisation increases with increasing initiator/stabiliser concentration. This is presumably because the more initiator/stabiliser is present the greater is the flux of free radicals available for the initiation of polymerisations. The reactions initiated by $FA(EO)_{45}Es$ and $FA(EO)_{60}Es$ resemble conventional emulsion polymerisation reactions so far as the shapes of the conversion-time curves are concerned (Figs. 6.7, 6.8). The rate also shows a general tendency to increase with an increase in initiator/stabiliser concentration.

7.2.3. Effect of temperature upon the shapes of the conversion-time curves and upon the rate of polymerisation. The next variable to be studied was temperature. The initiator/stabiliser concentration was maintained at 1.1×10^{-3} mol per 100 ml of water. The phase ratio of styrene to water was 40:100 by volume. Reactions initiated by $FA(EO)_{24}Es$ and $FA(EO)_{30}Es$ as initiator/stabiliser showed a remarkable variation in the shapes of the conversion-time curves (Figs. 6.9, 6.10). These curves range from those typical of bulk polymerisation at intermediate temperatures to those typical of conventional emulsion polymerisation at low temperatures. At high temperatures a new phenomenon was observed, namely, that of acceleration at a certain conversion (Figs. 6.9, 6.10). Since the shape of the curve sometimes

depends upon the concentration of the initiator/stabiliser, direct comparison of the rates is difficult. An attempt will be made later to explain the observed curves.

Emulsion polymerisations initiated by $FA(EO)_{45}Es$ and $FA(EO)_{60}Es$ have conversion-time curves typical of those for conventional emulsion polymrisation reactions (Figs. 6.11, 6.12), except that the linear section extends to high conversions in some cases before tailing off. As in conventional emulsion polymerisation reactions, the rate of polymerisation increases with increasing temperature, except at very high temperatures (ca. 65°C), when the rate tends to fall slightly.

7.2.4. Effect of initiator/stabiliser concentration upon the shapes of the conversion-time curves obtained when $FA(EO)_{24}Es$ and $FA(EO)_{30}Es$ were used as initiator/stabilisers at 45°C. Because the shape of the conversion-time curves obtained when $FA(EO)_{24}Es$ and $FA(EO)_{30}Es$ were used as initiator/stabilisers changed to that for emulsion polymerisation reactions when the reaction was carried out at temperatures below 50°C, the effect of initiator/stabiliser concentration upon the shape of the curve and upon the rate of polymerisation was investigated at the lower temperature of 45°C. The ratio of styrene to water by volume was 40:100. Figs. 6.13 and 6.14 show that curves typical of conventional emulsion polymerisation reactions were obtained even when only 4.0 g of $FA(EO)_{24}Es$ was used. In the case of reactions initiated by $FA(EO)_{30}Es$, conversion-time curves having shapes typical of conventional emulsion polymerisation reactions were observed when the level of initiator/stabiliser was as low as 3.0 g. In both cases, the rates of polymerisation increased with increasing initiator/stabiliser concentration.

7.2.5. Effect of increasing the total volume of water upon the shapes of conversion-time curves and upon the rates of polymerisation. The next variable whose effect was studied was the volume of water in the reaction system. Because some reactions at 50°C gave conversion-time curves which are not typical of those for conventional emulsion polymerisation reactions, the effect of varying the phase ratio was studied at 45°C. The concentration of initiator/stabiliser was 1.1×10^{-3} mol per 100 ml of

water.

In the case of $FA(EO)_{24}Fs$ as initiator/stabiliser at volume ratios of styrene to water of 40:72 and 40:100, the shapes of the curves chiefly resembled those typical of bulk polymerisation, although there seems to be an initial induction period present, as found in conventional emulsion polymerisation reactions (Fig. 6.15). At styrene-water volume ratios of 40:145 and 40:181 the shape of the curves was largely that of conventional emulsion polymerisation reactions. The fact that increasing the water volume at 45°C gave reaction systems which did not yield conversion-time curves typical of conventional emulsion polymerisations when $FA(EO)_{24}Fs$ was used as initiator/stabiliser may be due to the concentration of initiator in the water phase being too low to promote a conventional emulsion polymerisation reaction.

The curves for reactions initiated by $FA(EO)_{30}Fs$ had largely the shapes expected for an emulsion polymerisation reaction, and the curves given by $FA(EO)_{45}Fs$ and $FA(EO)_{60}Fs$ were independent of the monomer-water ratio in the range studied (Figs. 6.16-6.18).

The rates show a general tendency to increase when the volume of water is increased; however, the trend is not uniform. The general increase in rate is presumably due to an increase in the amount of initiator/stabiliser in the water phase. However, it was also observed that, when the monomer-water ratio was 40:72, the polymer conversion at a given time was greater than when the ratio of styrene to water was 40:100.

In general, the greater the volume of water, the greater the rate of polymerisation. However, in the case of $FA(EO)_{60}Fs$ there was no appreciable variation in the rate of polymerisation with increasing volume of water. This is perhaps an indication of the high water-solubility of $FA(EO)_{60}Fs$: an increase in the volume of water has little effect upon the amount dissolved in the water phase, and therefore little effect upon the rate of polymerisation.

7.2.6. Order of reaction with respect to concentration of initiator/stabiliser. In order to find the order of reaction with respect to

initiator/stabiliser concentration, the logarithm of the rate obtained from the straight-line portion of the conversion-time curves was plotted against the logarithm of the weight of initiator/stabiliser (Figs. 7.2a, b, c and d). Some of these plots are surprisingly good straight lines, though others are clearly not. The slopes of these plots are given below in Table 7.2:

Initiator/stabiliser	Order of reaction at 50°C	Order of reaction at 45°C
$FA(EO)_{24}Es$	2.05	1.5
$FA(EO)_{30}Es$	1.77	1.3 or 2.6*
$FA(EO)_{45}Es$	1.16	---
$FA(EO)_{60}Es$	0.80	---

*If the lowest concentration is not ignored.

Table 7.2: Order of reaction with respect to concentration of initiator/stabiliser at 50°C and at 45°C.

According to the Smith-Ewart theory, the order of reaction is 0.6 with respect to surfactant concentration and 0.4 with respect to initiator concentration. Since in the present work it is believed that one and the same substance functions as both initiator and stabiliser, orders of reaction close to unity ought to be observed if the Smith-Ewart mechanism is operative in this case. If one allows a certain margin for experimental error, the orders of reaction obtained for $FA(EO)_{45}Es$ and $FA(EO)_{60}Es$ could be regarded as being close to the theoretical prediction. However, the orders of reaction obtained for $FA(EO)_{24}Es$ and $FA(EO)_{30}Es$ are too high, and it seems that the assumptions of the Smith-Ewart theory are not completely valid for these two initiator/stabilisers. One of the assumptions of the Smith-Ewart theory is that the initiator is water-soluble. These initiator/stabilisers are indeed water-soluble, but they are also oil-soluble to an extent which depends upon the degree of ethoxylation. Not too surprisingly, the value of the order of reaction is lower when a conversion-time curve typical of conventional emulsion polymerisaton reactions is obtained, but it does not decrease enough to

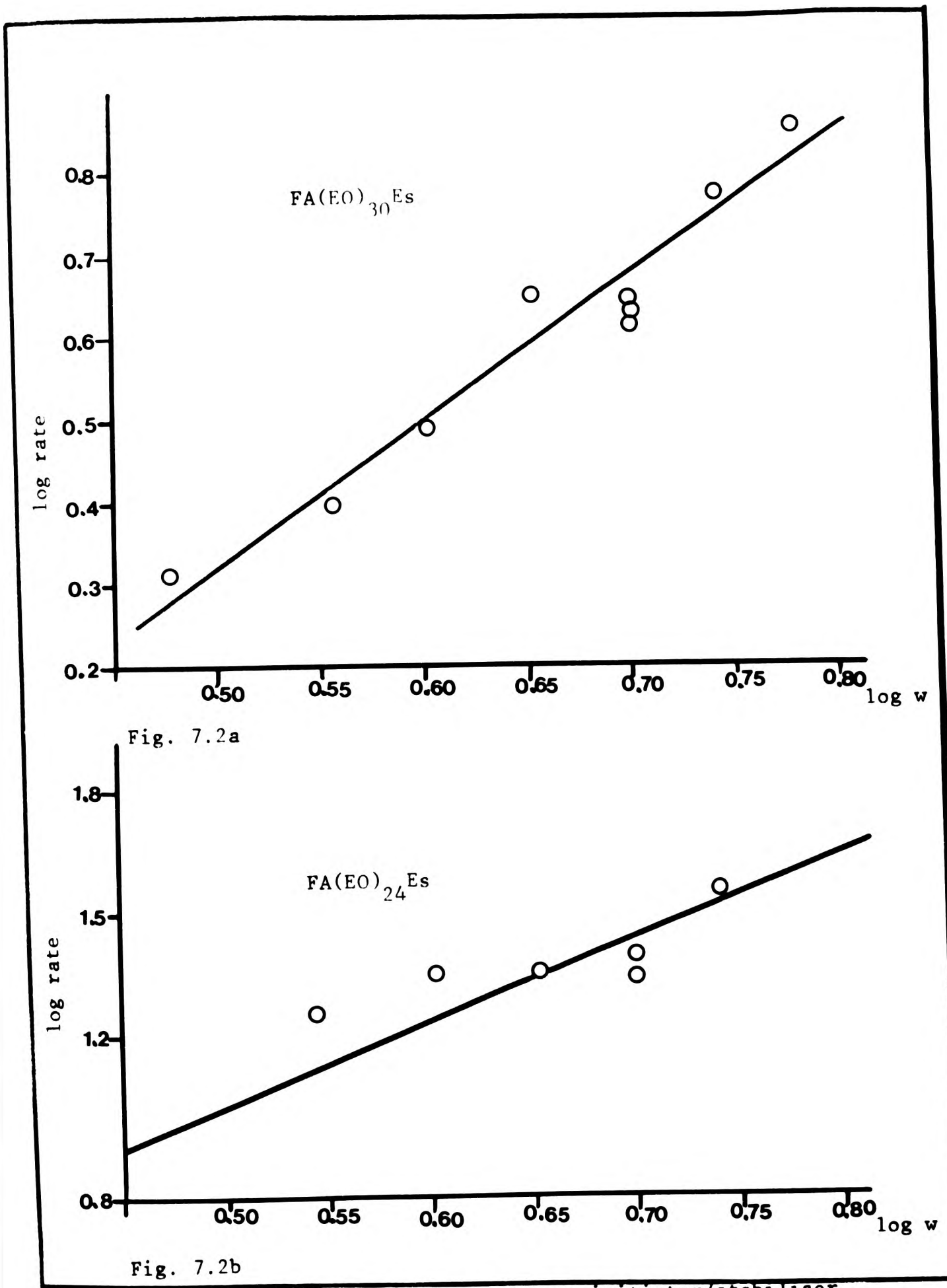


Fig. 7.2a

Fig. 7.2b

Figs. 7.2a and 7.2b: Log rate versus initiator/stabiliser concentration for reactions initiated and stabilised by $FA(EO)_{30}Es$ and $FA(EO)_{24}Es$ at $50^{o}C$.

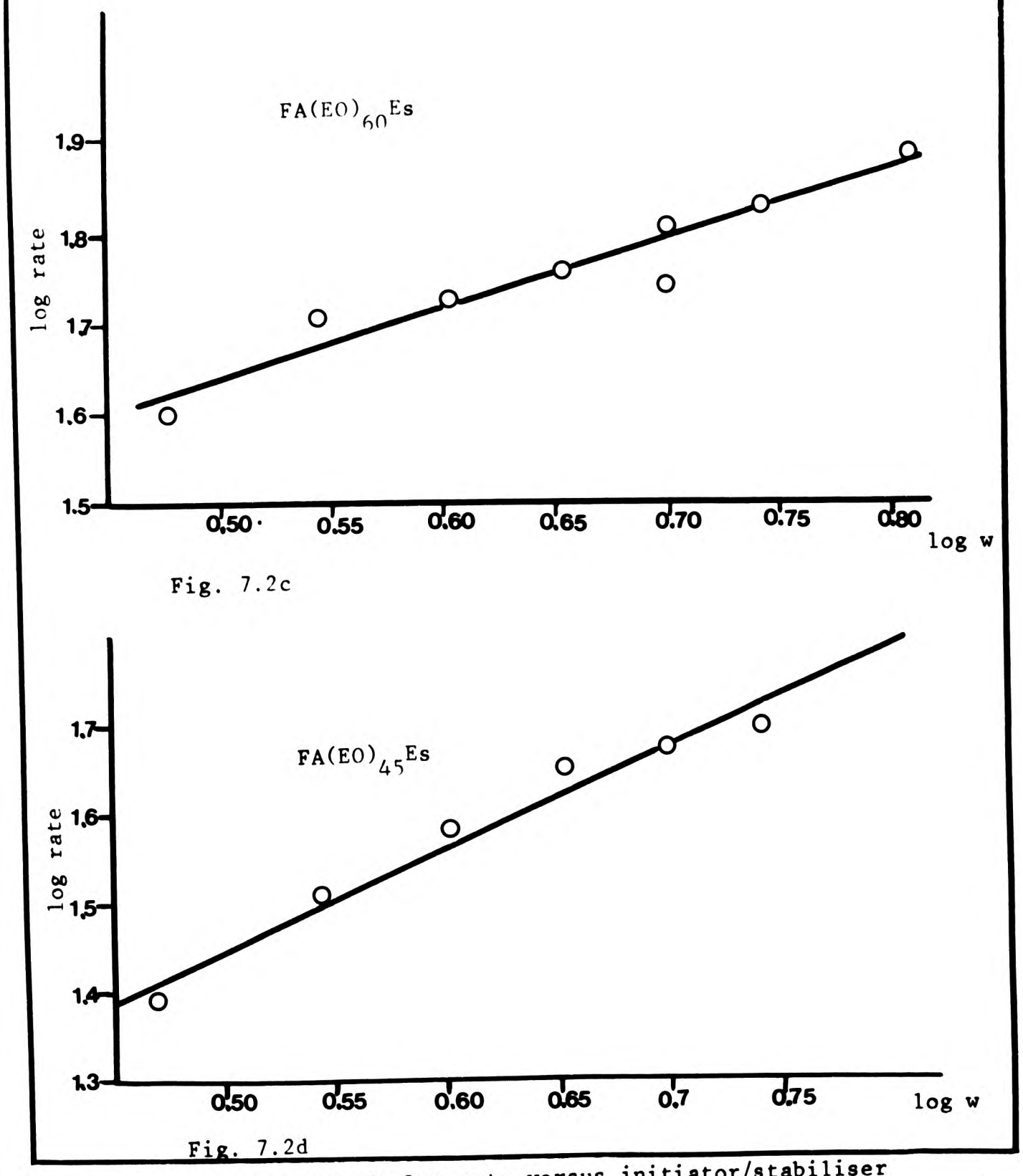


Fig. 7.2c

Fig. 7.2d

Figs. 7.2c and 7.2d: Log rate versus initiator/stabiliser concentration for reactions initiated and stabilised by $FA(EO)_{60}Es$ and $FA(EO)_{45}Es$ at $50^{o}C$.

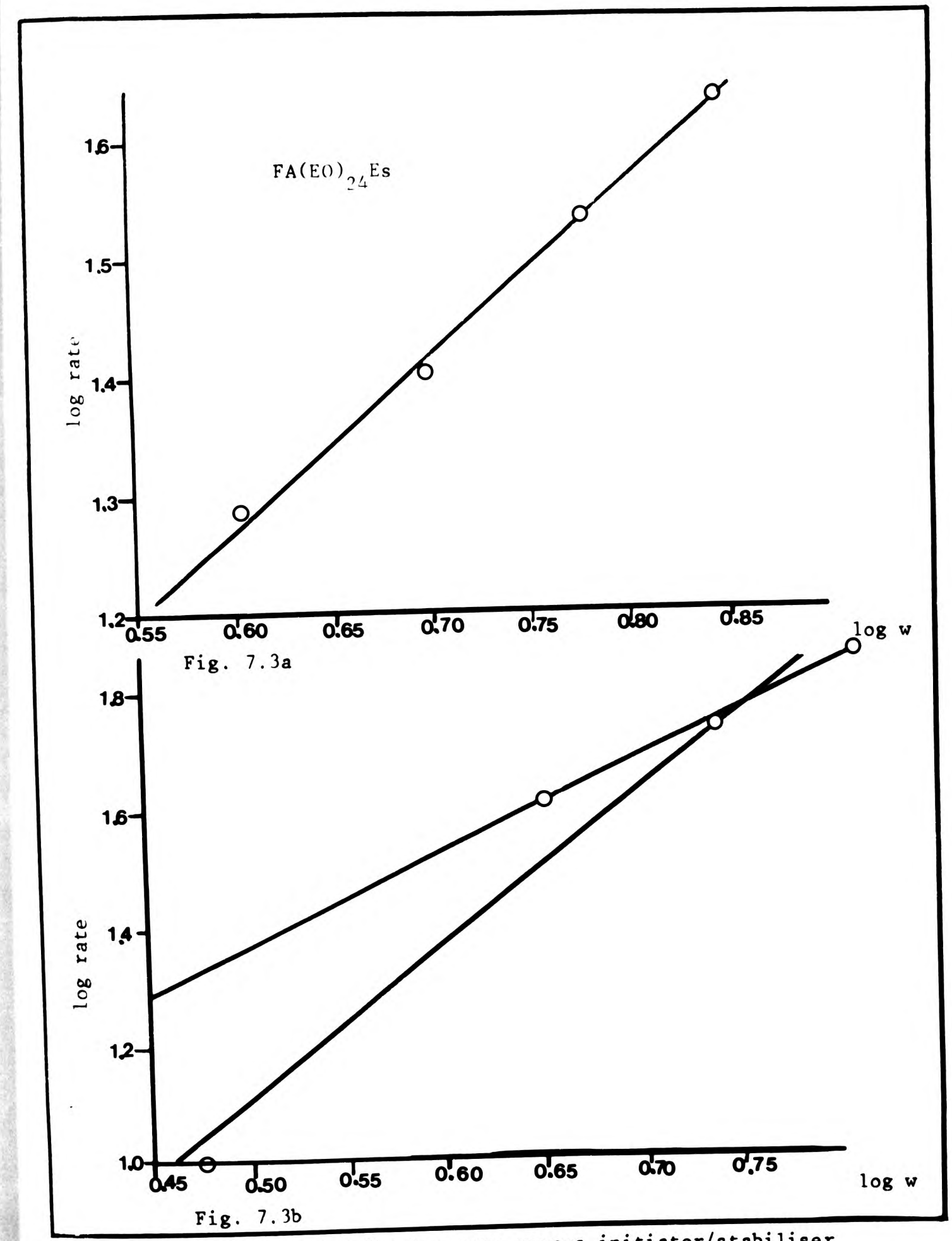


Fig. 7.3a

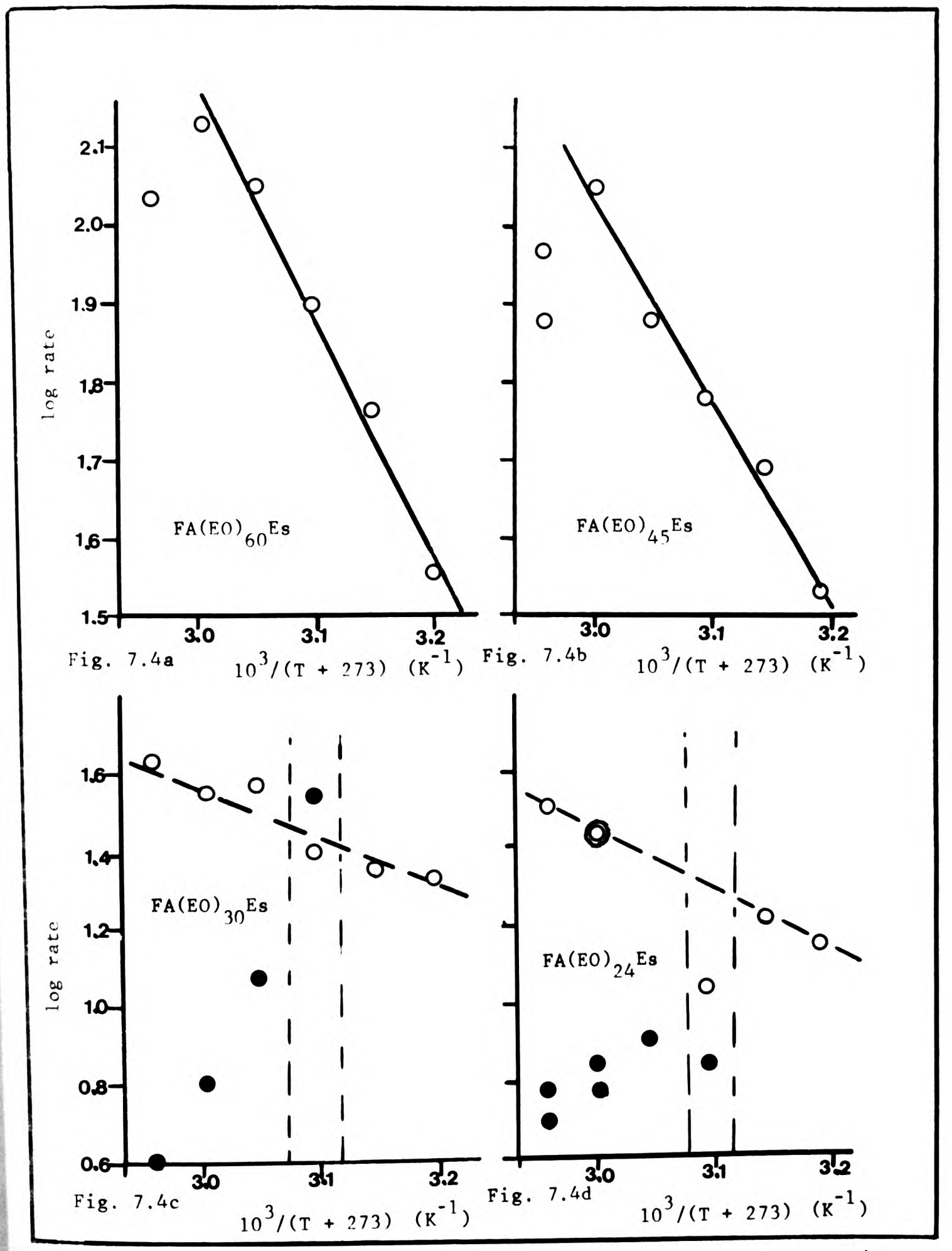
Fig. 7.3b

Figs. 7.3a and 7.3b: Log rate versus initiator/stabiliser concentration for reactions initiated and stabilised by $FA(EO)_{24}Es$ and $FA(EO)_{30}Es$ at $45^{o}C$.

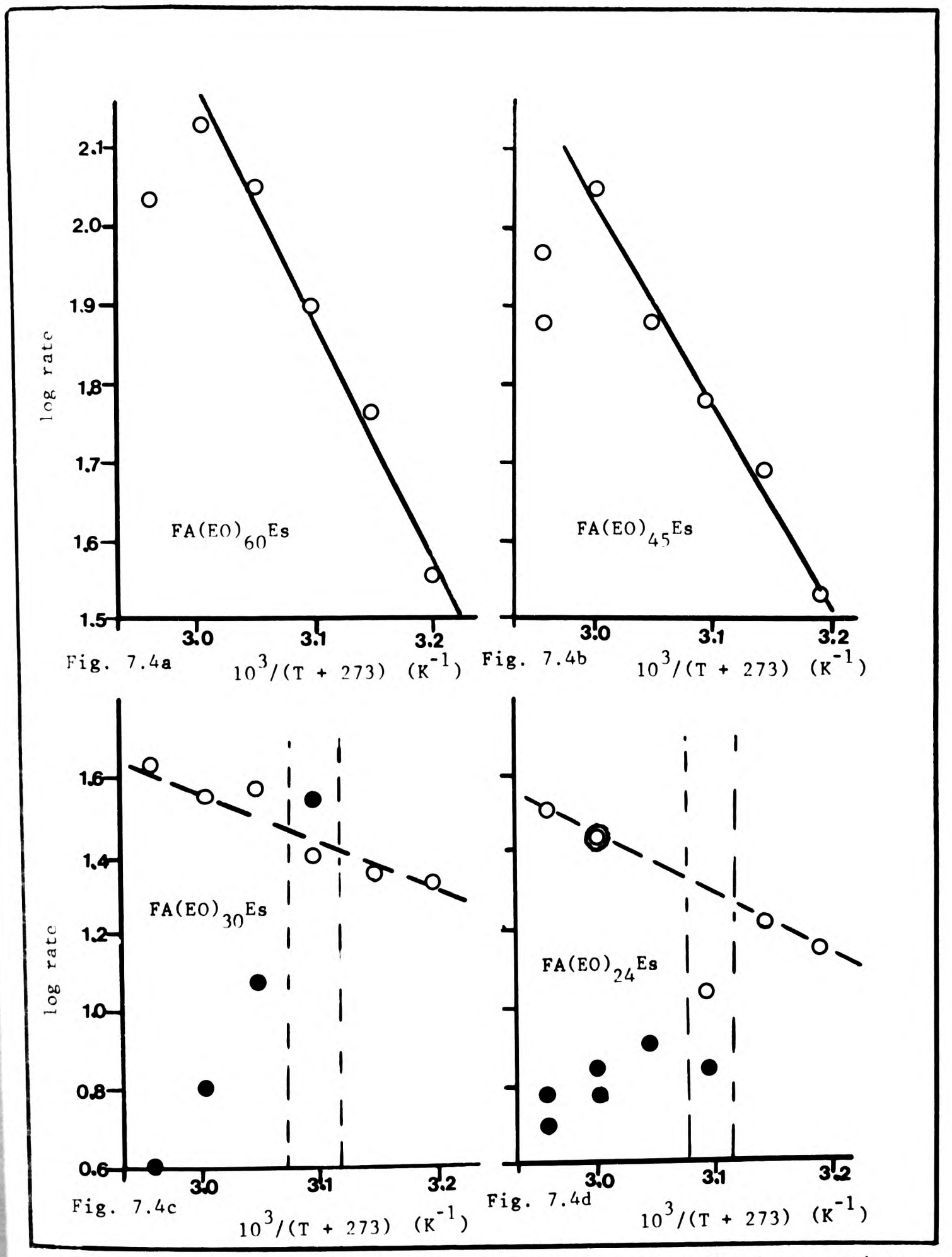
place $FA(EO)_{24}Es$ and $FA(EO)_{30}Es$ with $FA(EO)_{45}Es$ and $FA(EO)_{60}Es$, and thus it must be concluded that other factors are operative. As the initiator/stabiliser becomes more hydrophilic, so the order of reaction diminishes toward the Smith-Ewart prediction of one.

7.2.7. Calculation of activation energies. From the results of variation of rate of polymerisation with temperature, attempts were made to obtain activation energies from the Arrhenius plots. The equation used was that given in Chapter Six, section 6.8; i.e., the logarithm of the rate was plotted against the reciprocal absolute temperature. At first glance, it seems that the only valid results are those obtained with $FA(EO)_{45}Es$ and $FA(EO)_{60}Es$, since only for these initiator/stabilisers was there no change in the shape of the conversion-time curves observed at any of the polymerisation temperatures. Also, plots of the logarithm of the rate versus reciprocal temperature gives a single straight line of negative slope (Fig. 7.4). A slight "anomaly" is shown in reactions initiated by these compounds when at very high temperatures the rate falls below the value predicted by the Arrhenius relationship. These values are not taken into consideration when calculating the energy of activation. An attempt will be made later to explain this phenomenon. The results, however, are more complicated for reactions initiated by $FA(EO)_{24}Es$ and $FA(EO)_{30}Es$, since the Arrhenius plots are two straight lines, one of positive slope, the other of negative slope; this is presumably a consequence of the shapes of the conversion-time curves. It could easily be concluded that the fact that some points for the reactions initiated by $FA(EO)_{24}Es$ and $FA(EO)_{30}Es$ lie on a straight line of negative slope is coincidental, since the points that make up the straight line come from slopes of conversion-time curves having very different shapes (Fig. 7.5).

The conversion-time curves of these reactions can be divided into three distinct portions (Fig. 7.5). At low temperatures, i.e., 40-45°C, the shape is that typical of a conventional emulsion polymerisation reaction, and only one rate is observed. At 50°C two straight portions are obtained, the first being of higher slope and the second straight portion of lower slope. Results given in Tables 6.8 and 6.9 and discussed later show that the number of particles decreases during the first linear portion but remains constant within experimental error for the second, slower, linear portion.



Figs. 7.4a,b,c,d: Arrhenius plots for emulsion polymerisation reactions initiated and stabilised by 1.1×10^{-3} mol of $FA(EO)_{24}Es$, $FA(EO)_{30}Es$, $FA(EO)_{45}Es$ and $FA(EO)_{60}Es$.



Figs. 7.4a,b,c,d: Arrhenius plots for emulsion polymerisation reactions initiated and stabilised by 1.1×10^{-3} mol of $FA(EO)_{24}Es$, $FA(EO)_{30}Es$, $FA(EO)_{45}Es$ and $FA(EO)_{60}Es$.

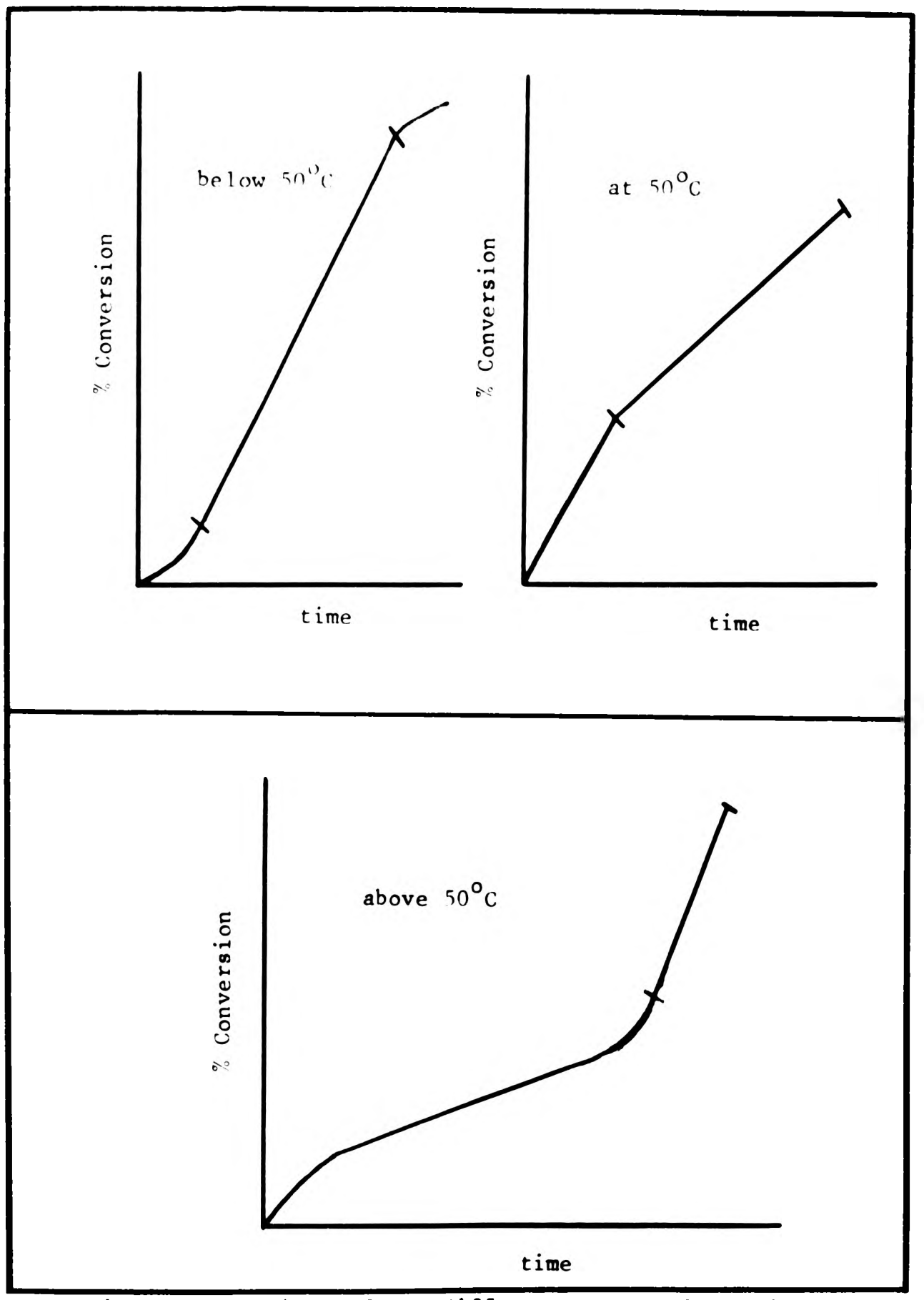


Fig. 7.5: Portions of the different curves whose slopes were used to make the Arrhenius plots for reactions initiated by $FA(EO)_{24}Es$ and $FA(EO)_{30}Es$.

Above 50°C, again two constant-rate regions are observed. The number of particles remains constant within experimental error during the first portion of the curve. Unfortunately, not enough data are available for particle numbers for the reaction during the second linear stage.

For temperatures below 50°C, only one linear region is observed in each reaction and the rates corresponding to these linear regions fall on Arrhenius plots of negative slope. These points are typical of conventional emulsion polymerisation behaviour. For the results at 50°C, the points that lie on the Arrhenius plot of negative slope derive from the linear portion corresponding to a constant number of particles (Fig. 7.5), i.e., the second linear portion. For temperatures above 50°C, the points lying on the Arrhenius plot of negative slope represent the rates after acceleration takes place.

The activation energies obtained from the Arrhenius plots are given in Table 7.3:

Initiator/stabiliser	Activation energy (kJ mol^{-1}) (styrene:water 40:100)
$FA(EO)_{24}Es$	29.7
$FA(EO)_{30}Es$	23.3
$FA(EO)_{45}Es$	49.6
$FA(EO)_{60}Es$	58.3

Table 7.3: Activation energies obtained for the emulsion polymerisation of styrene using $FA(EO)_{24}Es$, $FA(EO)_{30}Es$, $FA(EO)_{45}Es$ and $FA(EO)_{60}Es$ as initiator/stabilisers. Styrene:water = 40:100.

Though the trend is not monotonic, there is an overall increase in activation energy with increasing size of the initiator/stabiliser molecule. However, no conclusions can be drawn from this observation, since the activation energy depends upon the rate of initiation and upon the rate of propagation; the rates of initiation were shown in Section 7.2.1 to be largely similar for all the esters, while the rate of propagation depends upon the number of particles N generated, and this has been shown to vary in a complex fashion, not only as between one ester and another, but also

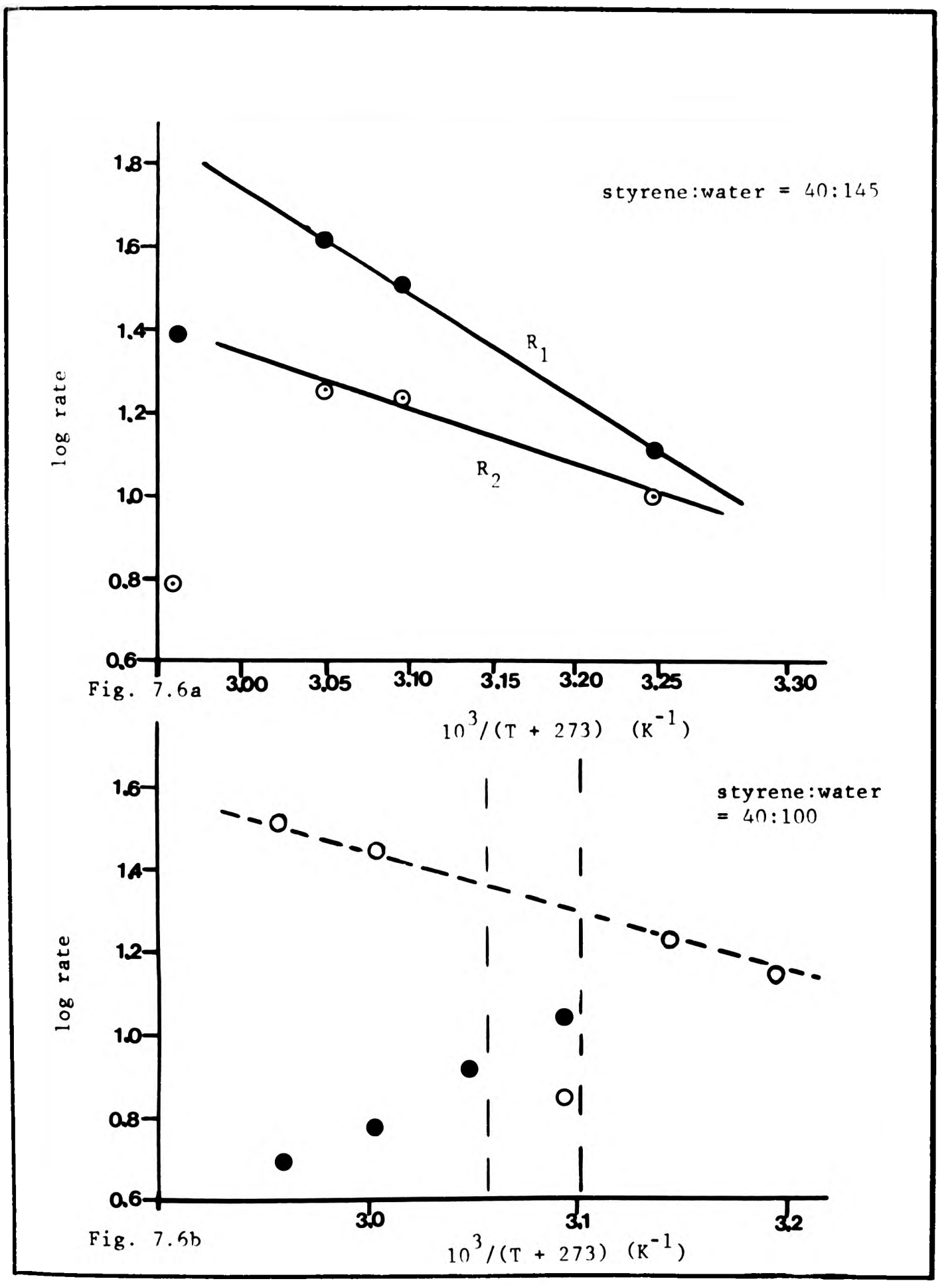


Fig. 7.6a

Fig. 7.6b

Figs. 7.6a,b: Arrhenius plots for emulsion polymerisation reactions initiated and stabilised by 1.1×10^{-3} mol of $FA(EO)_{24}Es$ with styrene:water ratios of 40:145 and 40:100.

at different temperatures with a single ester.

It is interesting to note that at high temperatures the rate of reaction for the first portion of the curve decreases as the temperature increases for both $FA(EO)_{24}Es$ and for $FA(EO)_{30}Es$. Electron micrographs show that N, the number of particles, decreases as the temperature increases for the first portion of the curve.

The effect of temperature was studied once again for the reaction initiated by $FA(EO)_{24}Es$ with an increased volume of water. The styrene:water ratio was 40:145 by volume and the amount of initiator/stabiliser was 1.1×10^{-3} mol per 40 ml of styrene. All the results from these experiments gave conversion-time curves of similar shapes (Fig. 6.19). The curves consist of two linear portions. The first linear portion had the higher rate, denoted by R_1. The second, subsequent, straight-line rate was slower and is denoted by R_2. Activation energies were obtained for the two rates. The results are given in Table 7.4 and in Fig. 7.6.

Initiator/stabiliser	Activation energy (kJ mol^{-1}) (styrene:water 40:145)
$FA(EO)_{24}Es$	48.1 (R_1) 25.6 (R_2)

Table 7.4: Activation energies obtained for the emulsion polymerisation of styrene using $FA(EO)_{24}Es$ as initiator/stabiliser. Styrene:water = 40:145.

The value given for R_1 is not valid as a measure of activation energy, since, as stated above, the number of particles varies during the first portion of the conversion-time curve.

7.2.8. Dependence of the rate upon the volume of water. Plots of rate of polymerisation against styrene:water ratio obtained from the conversion-time curves gave straight lines whose slopes increased as the number of oxyethylene units in the initiator/stabiliser decreased (Fig. 7.7). The results obtained are given in Table 7.5:

Initiator/stabiliser	Slope (% h^{-1})
$FA(EO)_{24}Es$	8.6
$FA(EO)_{30}Es$	4.1
$FA(EO)_{45}Es$	1.3
$FA(EO)_{60}Es$	1.0

Table 7.5: Dependence of rate upon the volume of water.

These results show that $FA(EO)_{24}Es$, with the fewest oxyethylene groups per molecule, shows a strong dependence upon the amount of water present: the more water present, the greater the rate of conversion. As the number of oxyethylene groups per molecule increases, this dependence upon volume of water decreases, until with $FA(EO)_{60}Es$ one finds that the rate is independent of the amount of water. Such results are consistent with the indirect evidence given throughout this chapter suggesting that the solubility of the esters in water increases with an increasing number of oxyethylene groups in the molecule: with $FA(EO)_{24}Es$, for example, the solubility in water is sufficiently low that an increase in the volume of water present yields a significant increase in the amount of ester in the water phase, whereas the water solubility of $FA(EO)_{60}Es$, in contrast, is so high that increasing the volume of water makes little difference to the amount of ester present in the water phase.

7.2.9. Surfactant properties of $FA(EO)_{30}H$, $FA(EO)_{60}H$ and their corresponding esters. The surfactant properties of $FA(EO)_{30}H$ and $FA(EO)_{60}H$ and the esters derived from 4,4'-AB-4-CPA and these fatty-alcohol ethoxylates were studied (Figs. 6.21 and 6.22). The cmc value of $FA(EO)_{30}H$ was found to be 1.24×10^{-5} mol/l (literature value 2.20×10^{-5} mol/l[179]). The cmc value of $FA(EO)_{60}H$ was 4.35×10^{-6} mol/l (literature value 1.20×10^{-5} mol/l[179]). The discrepancies between observed values and literature values are probably to be attributed to the fact that the fatty-alcohol ethoxylates used are not pure substances, but mixtures incorporating a range of numbers of oxyethylene units. However, both $FA(EO)_{30}Es$ and $FA(EO)_{60}Es$ failed to yield a curve from which a cmc value could be obtained.

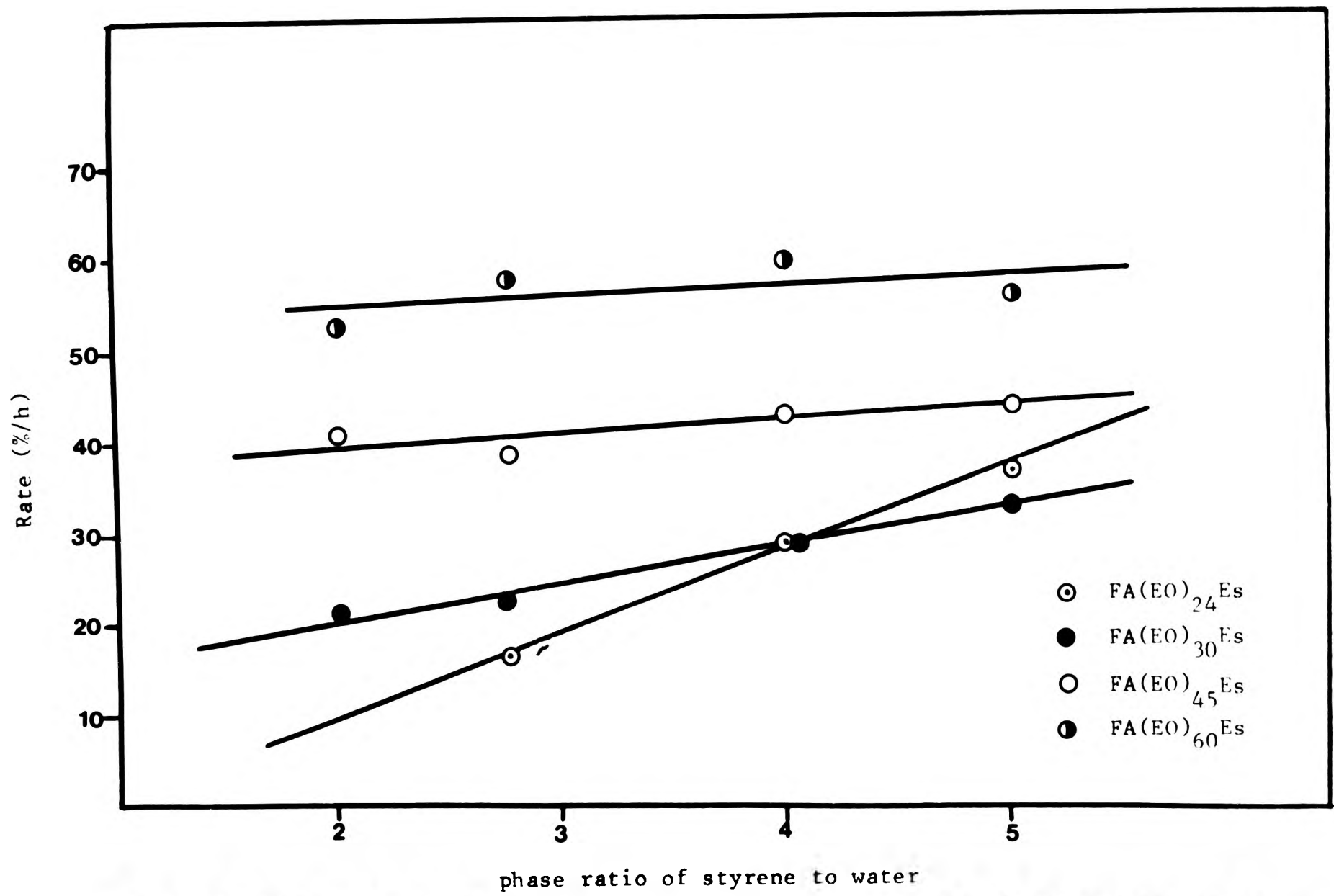


Fig. 7.7: Effect of changing the volume of water upon the rate of polymerisation of styrene using $FA(EO)_{24}Es$, $FA(EO)_{30}Es$, $FA(EO)_{45}Es$ and $FA(EO)_{60}Es$ as initiator/stabilisers.

This failure of the esters to yield cmc values, in contrast with the behaviour of the corresponding fatty-alcohol ethoxylates, can be expiained if one considers the structures of their molecules. The fatty-alcohol ethoxylates, which have the general formula $C_{17}H_{33}(OC_2H_4)_nOH$, have a clearly-defined hydrophobic end and a clearly-defined hydrophilic end, and are thus in principle free to form micelles. The esters, however, have the general formula $[C_{17}H_{33}(OC_2H_4)_nO_2CC_2H_4C(CN)(CH_3)N=]_2$, that is, they exhibit alternating hydrophobic and hydrophilic moieties, with a hydrophobic moiety at each end. Such a structure is unlikely to be able to form micelles easily, and hence a cmc value will be difficult to determine.

7.2.10. Particle-size measurements. Particle-size measurements were carried out using two different techniques. One of the methods involved the use of a Coulter Nanosizer apparatus; the other used the electron microscope.

It has been observed that the Coulter Nanosizer is a good technique to use in the case of final latices when no new nucleation has taken place during the later stages of polymerisation. It is also suitable for following the course of particle growth, except at the onset of the reaction, when the Nanosizer does not register very small particles, i.e., smaller than 70 nm. This method has the advantage that thousands of particles are assayed in a few minutes. Also, comparison with electron microscopic techniques for those samples with which both techniques were used showed remarkable agreement, except when new particles were generated in the later stages of the polymerisation.

The electron microscope technique taking pictures from a copper grid on which a drop of latex diluted many times is placed. For hard polymers which suffer no distortion on drying, which are neither expanded nor contracted by irradiation with electrons and which are monodisperse, the electron microscope gives results of high accuracy[197]. Unfortunately, the time required for manual sizing and counting has the effect of limiting the measurement to 1000 or fewer particles in some cases. These numbers are perfectly adequate for monodisperse latices but are likely to be inadequate where significant polydispersity exists. Also, this technique

has the drawback that big particles take a certain place in the grid (usually the centre), while the smaller particles tend to move towards the periphery of the grid. The calculated number of particles then may depend upon the part of the grid which has been selected for taking the picture.

Fig. 7.8: Pictures of the latex produced using $FA(EO)_{30}Es$ at 40°C as initiator/stabiliser, showing variation in the proportion of particles of different sizes in different regions of the same grid.

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Fig. 7.8: Pictures of the latex produced using $FA(EO)_{30}Es$ at 40°C as initiator/stabiliser, showing variation in the proportion of particles of different sizes in different regions of the same grid.

The electron microscope technique possesses the great advantage over the Coulter Nanosizer that it shows a new crop of particles at the time it occurs. This, of course, does not mean that it is always possible to measure accurately early reaction particles. Table 7.6 shows the number of particles obtained using both methods.

Initiator/stabiliser	Number of particles N (l^{-1})		
	Nanosizer	Electron microscope	
$FA(EO)_{30}Es$ (60°C)	8.64×10^{16}	7.31×10^{16}	1.45×10^{16}
$FA(EO)_{60}Es$ (60°C)	6.60×10^{17}	4.33×10^{17}	0.67×10^{17}
$FA(EO)_{60}Es$ (40°C)	4.72×10^{17}	5.26×10^{17}	1.64×10^{17}
$FA(EO)_{24}Es$ (60°C)	6.21×10^{16}	4.91×10^{16}	0.66×10^{16}
$FA(EO)_{30}Es$ (40°C)	1.83×10^{17}	2.54×10^{17}	0.25×10^{17}

Table 7.6: Concentration of latex particles found using (i) a Coulter Nanosizer and (ii) an electron microscope.

Considering the limitations of the Coulter Nanosizer and of the electron microscope, the agreement between the two methods is satisfactory.

The effect of the concentration of the initiator/stabiliser upon the number of particles in the latex, the effect of temperature and the effect of increasing the volume of water upon the number of particles were determined using the Coulter Nanosizer.

7.2.11. Effect of initiator/stabiliser concentration upon the number of particles. The first variable to be investigated was the effect upon the number of particles in the latex of the concentration of initiator/stabiliser. The measurements were taken at the end of the reaction. In all four cases, i.e., when either $FA(EO)_{24}Es$, $FA(EO)_{30}Es$, $FA(EO)_{45}Es$ or $FA(EO)_{60}Es$ was used as initiator/stabiliser, it was found that in general the number of particles increased slightly as the concentration of initiator/stabiliser increased. Fig. 7.8 shows plots of log N versus log weight of initiator/stabiliser. Table 7.7 gives the slopes of plots of log N versus log weight of initiator/stabiliser.

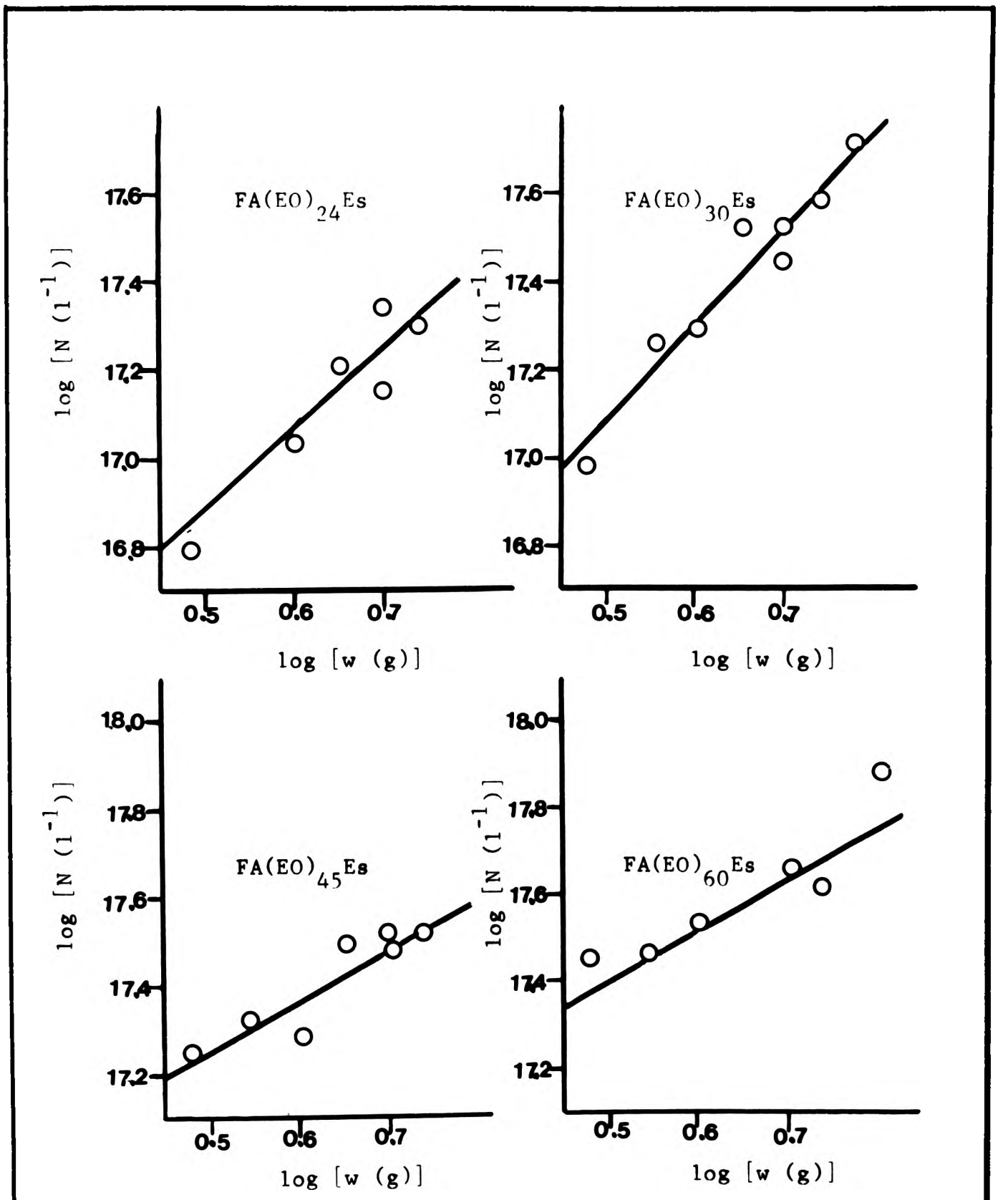

Fig. 7.8: Effect of concentration of initiator/stabiliser on particle number at 50°C.

Initiator/stabiliser	Slope (50°C)	Slope (45°C)
$FA(EO)_{24}Es$	1.83	1.94
$FA(EO)_{30}Es$	2.19	2.20
$FA(EO)_{45}Es$	1.13	---
$FA(EO)_{60}Es$	1.17	---

Table 7.7. Slopes obtained from plots of log N versus log weight of initiator/stabiliser using Nanosizer.

Reproducibility studies on particle numbers gave the following results.

Initiator/stabiliser	Mass (g)	N (l^{-1})
$FA(EO)_{24}Es$	5.0	1.43×10^{17} 2.21×10^{17}
$FA(EO)_{60}Es$	5.0	4.63×10^{17} 4.67×10^{17}

Table 7.8. Reproducibility of particle numbers when using $FA(EO)_{24}Es$ and $FA(EO)_{60}Es$ as initiator/stabilisers using Nanosizer.

The results given in Table 7.8 were obtained at different conversions. However, it will become clear later that comparisons between the values are valid, because after a certain point conversion has little effect upon particle number.

7.2.12. Effect of temperature upon particle numbers. The effect of temperature upon the number of particles generated revealed a rather unexpected trend. As can be seen from Fig. 7.1, there is a division in the shapes of the conversion-time curves of the emulsion polymerisation of styrene when the different esters are used as initiator/stabilisers. Fig. 7.9 shows that for reactions initiated by $FA(EO)_{24}Es$ and $FA(EO)_{30}Es$ the particle numbers steadily increase as the temperature decreases. The variation resembles an Arrhenius relationship, i.e., log N varies linearly with 1/T, except that the slope is positive instead of negative. However, for reactions initiated by $FA(EO)_{45}Es$ and $FA(EO)_{60}Es$, the particle number initially increases with increasing temperature, followed by a decrease in the number of particles with further increase in the

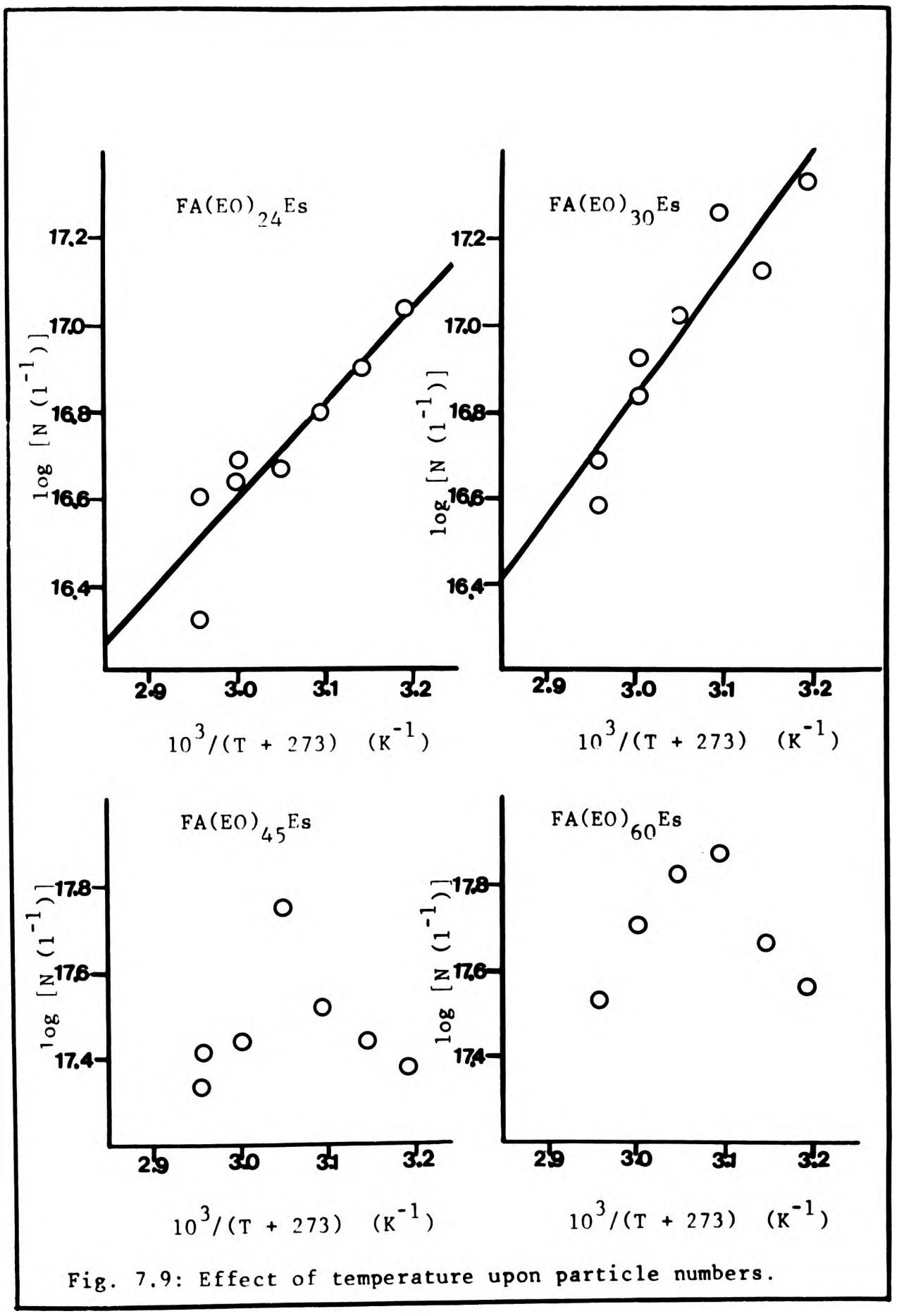

Fig. 7.9: Effect of temperature upon particle numbers.

temperature. It should be borne in mind that these particle size measurements were carried out using a Coulter Nanosizer. The effect of temperature on numbers of particles generated is more complex than shown here, and an attempt will be made later to explain the observed phenomena.

Fig. 7.10 shows the effect of increasing the volume of water upon the number of particles for reactions initiated and stabilised by $FA(EO)_{24}Es$.

7.2.13. Effect of increasing volume of water upon particle numbers. The effect of increasing the volume of water in the polymerisation reaction system upon the number of particles generated is shown in Fig. 7.13. The total number of particles per litre remains constant for the reactions initiated by $FA(EO)_{60}Es$ and $FA(EO)_{30}Es$. The latices prepared using $FA(EO)_{45}Es$ and $FA(EO)_{24}Es$ show an increase in the number of particles with increasing volume of water. These results are surprising, since one would expect the number of particles to be more sensitive to the volume of water with $FA(EO)_{24}Es$ and $FA(EO)_{30}Es$ than with $FA(EO)_{45}Es$ and $FA(EO)_{60}Es$, because the latter are more hydrophilic, and yet one finds a quite different grouping of the esters. The reader should bear in mind that these particle-number measurements were carried out using the Nanosizer, which fails to register small particles.

7.2.14. Effect of number of ethylene oxide units in the initiator/stabiliser upon particle numbers. Fig. 7.14 shows that the number of particles increases as the number of ethylene oxide units in the initiator/stabiliser increases. The increase in the number of particles is particularly marked in series of experiments in which the molar level of initiator/stabiliser was held constant. This is to be expected, since not only does the relative solubility of the esters in water increase as the polyoxyethylene chain length increases, but the amount of initiator/stabiliser increases at the same time, since the molecular weight of the ester increases. Thus, more ester is available to dissolve in the water phase, and this presumably results in an increase in the number of particles nucleated.

7.3. Detailed discussion of results and conclusions. In order to elucidate a mechanism for the emulsion polymerisation of styrene when the fatty-

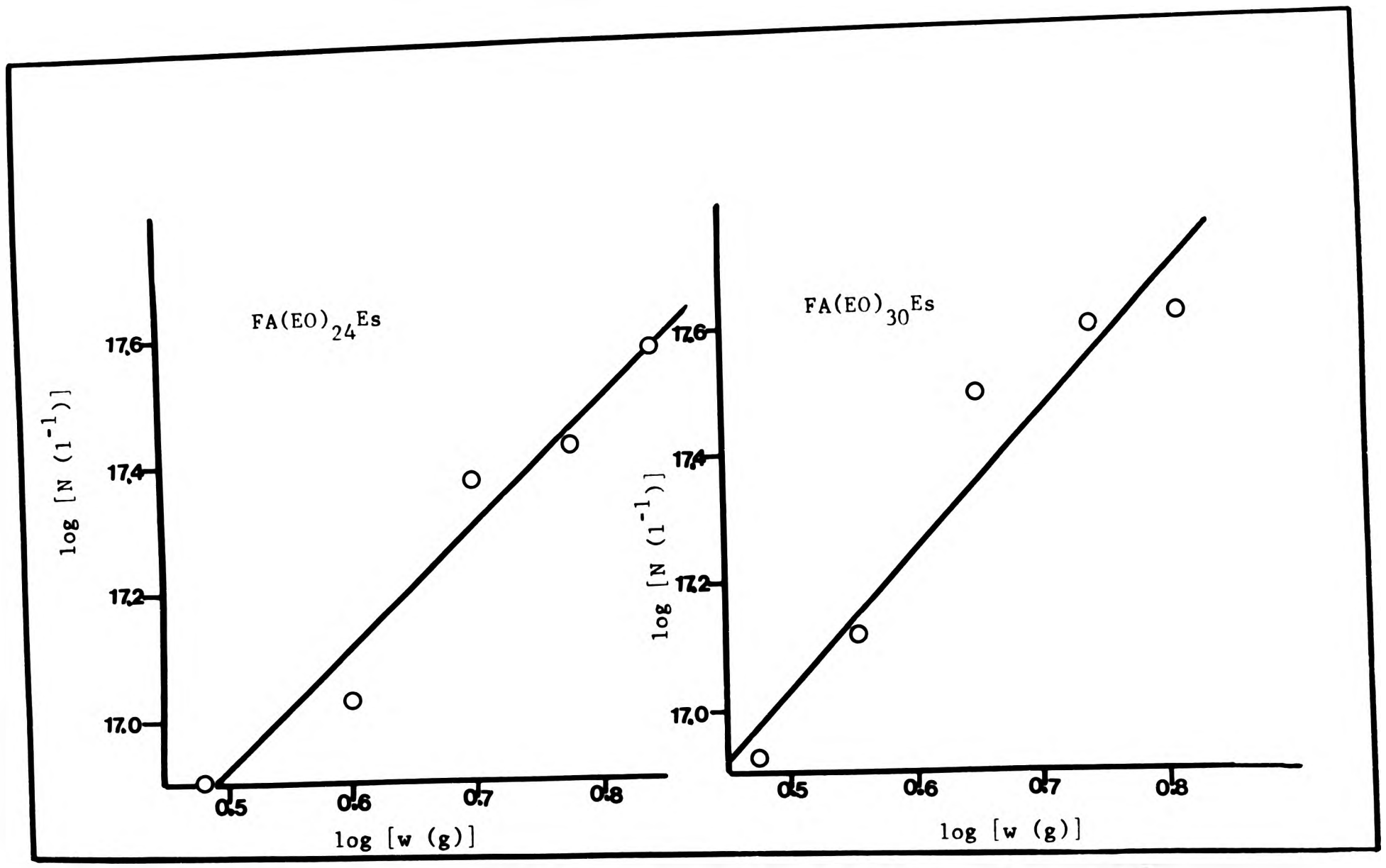

Fig. 7.10: Effect of initiator/stabiliser concentration on particle numbers at 45°C.

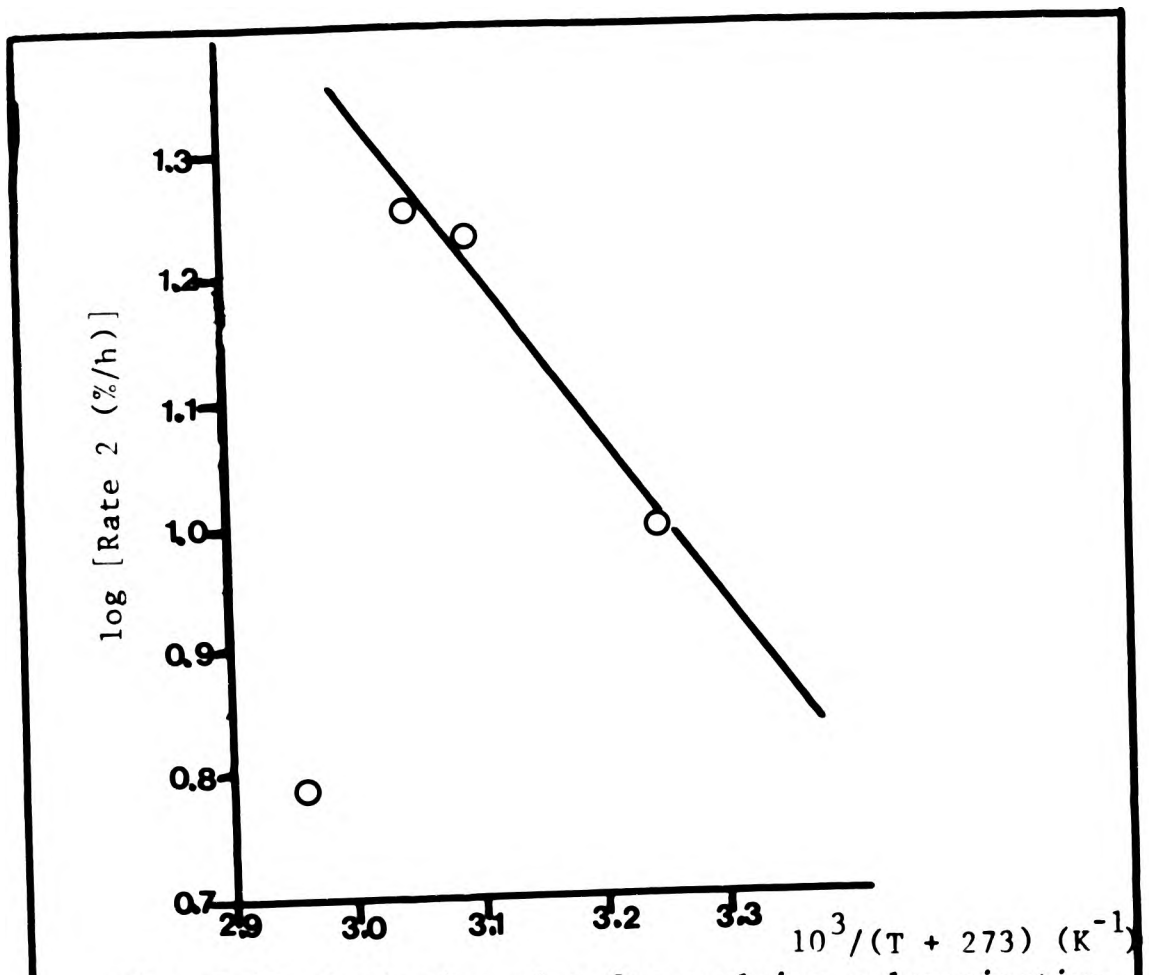

Fig. 7.11: Arrhenius plot for emulsion polymerisation reactions initiated and stabilised by $FA(EO)_{24}Es$ at a styrene:water volume ratio of 40:145.

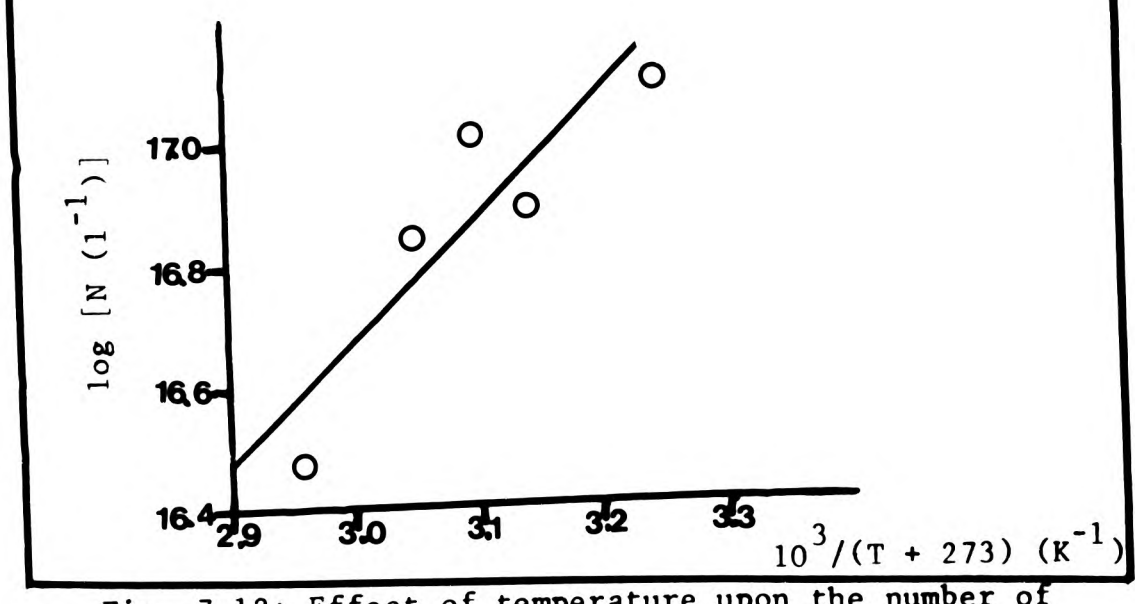

Fig. 7.12: Effect of temperature upon the number of particles when $FA(EO)_{24}Es$ is used as initiator/ stabiliser at a styrene:water volume ratio of 40:145.

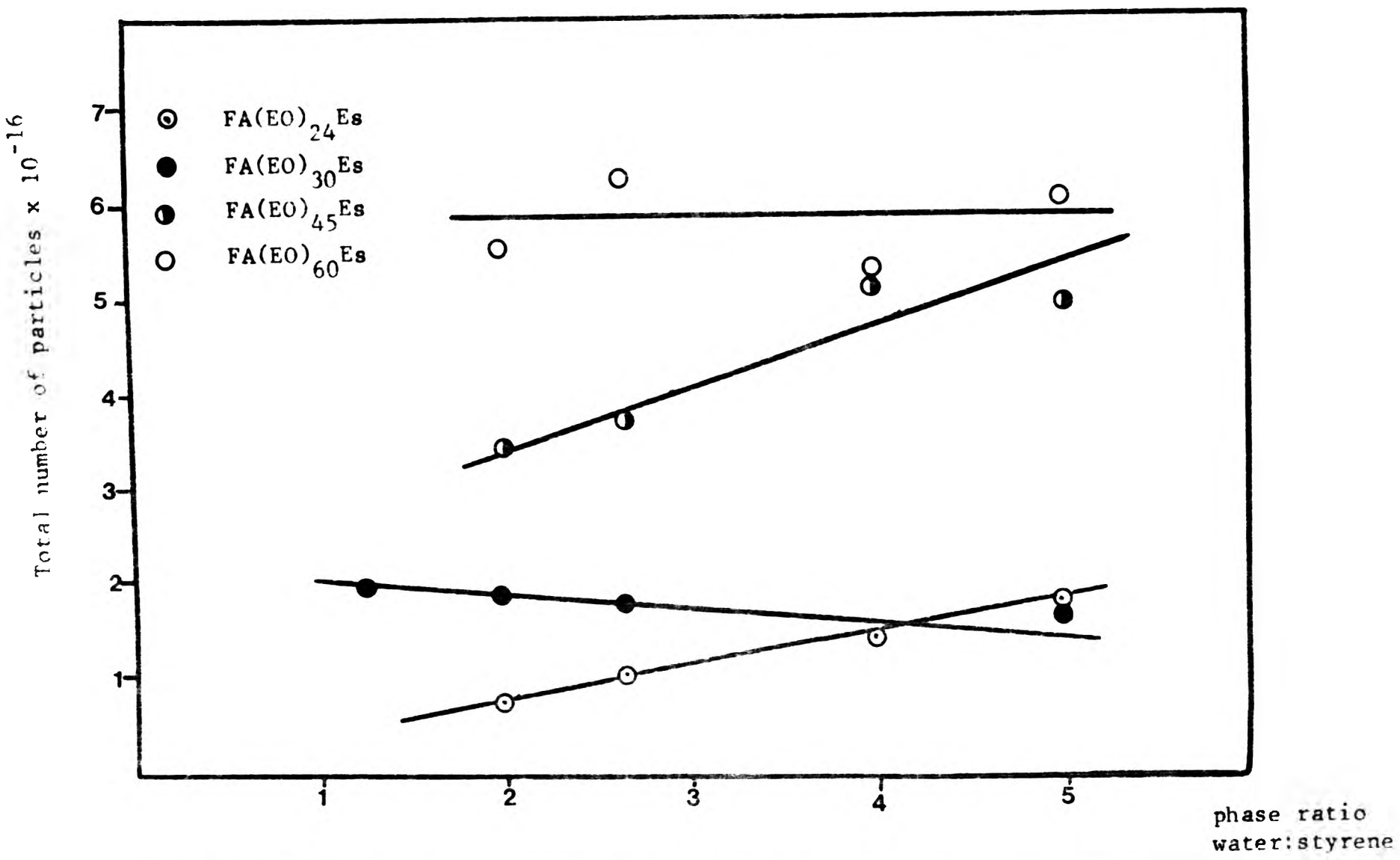

Fig. 7.13: Effect of increasing the volume of water upon the number of particles.

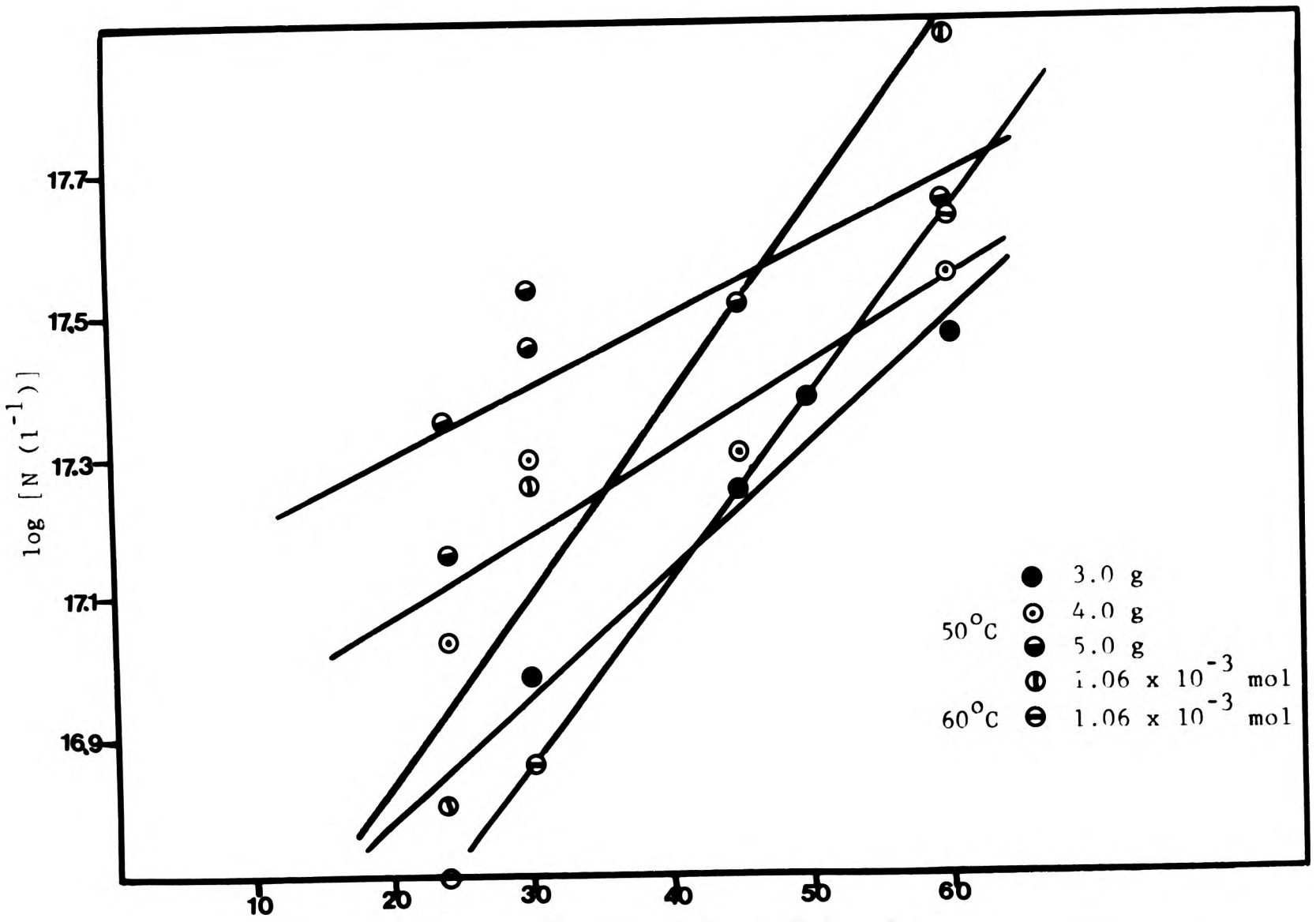

Fig. 7.14: Effect of the average number of ethylene oxide units in the ester molecule upon the number of particles.

alcohol ethoxylate esters of 4,4'-AB-4-CPA were used as initiator/stabilisers which would account for the observed results, a few experiments were devised in which the growth of the polymer particles was followed as the reaction proceeded. Both the electron micrograph technique and the Coulter Nanosizer were used to measure particle diameters. The recipe used was that given in Chapter Six, Section 6.2.2. These experiments were as follows:

Initiator/stabiliser	Temperature (°C)	Whether acceleration observed*
$FA(EO)_{60}Fs$	60	no
$FA(EO)_{60}Fs$	40	no
$FA(EO)_{30}Fs$	60	yes
$FA(EO)_{30}Fs$	40	no
$FA(EO)_{24}Fs$	60	yes

*The sudden rapid increase in the polymerisation rate at high conversions is called 'acceleration'.

Table 7.9: Experiments carried out for in-depth study.

Table 6.9 gives the average particle diameters obtained using the electron microscope and the Coulter Nanosizer. The sample given in Table 6.9 is the average particle diameters obtained for polystyrene latices when $FA(EO)_{30}Fs$ was used as initiator/stabiliser. The temperature of the reaction was 60°C. The electron micrographs show a steady increase in the average diameter for most of the reaction, but near the end of the reaction there is a drop in the average diameter. The Coulter Nanosizer does not register the small new particles generated near the end of the reaction. Thus, the tables of particle numbers given in Chapter Six have to be considered with this in mind. The electron micrographs show that secondary nucleation of particles occurs at approximately 60% conversion. When $FA(EO)_{30}Fs$ is used at 40°C, both methods show a steady increase in the average diameter; no secondary crop of particles is observed. The polymerisation initiated by $FA(EO)_{60}Es$ shows no new generation of particles within experimental error at either temperature. The polymerisation initiated by $FA(EO)_{24}Es$ at 60°C shows again that new particles are generated at approximately 65% conversion. Particle-size

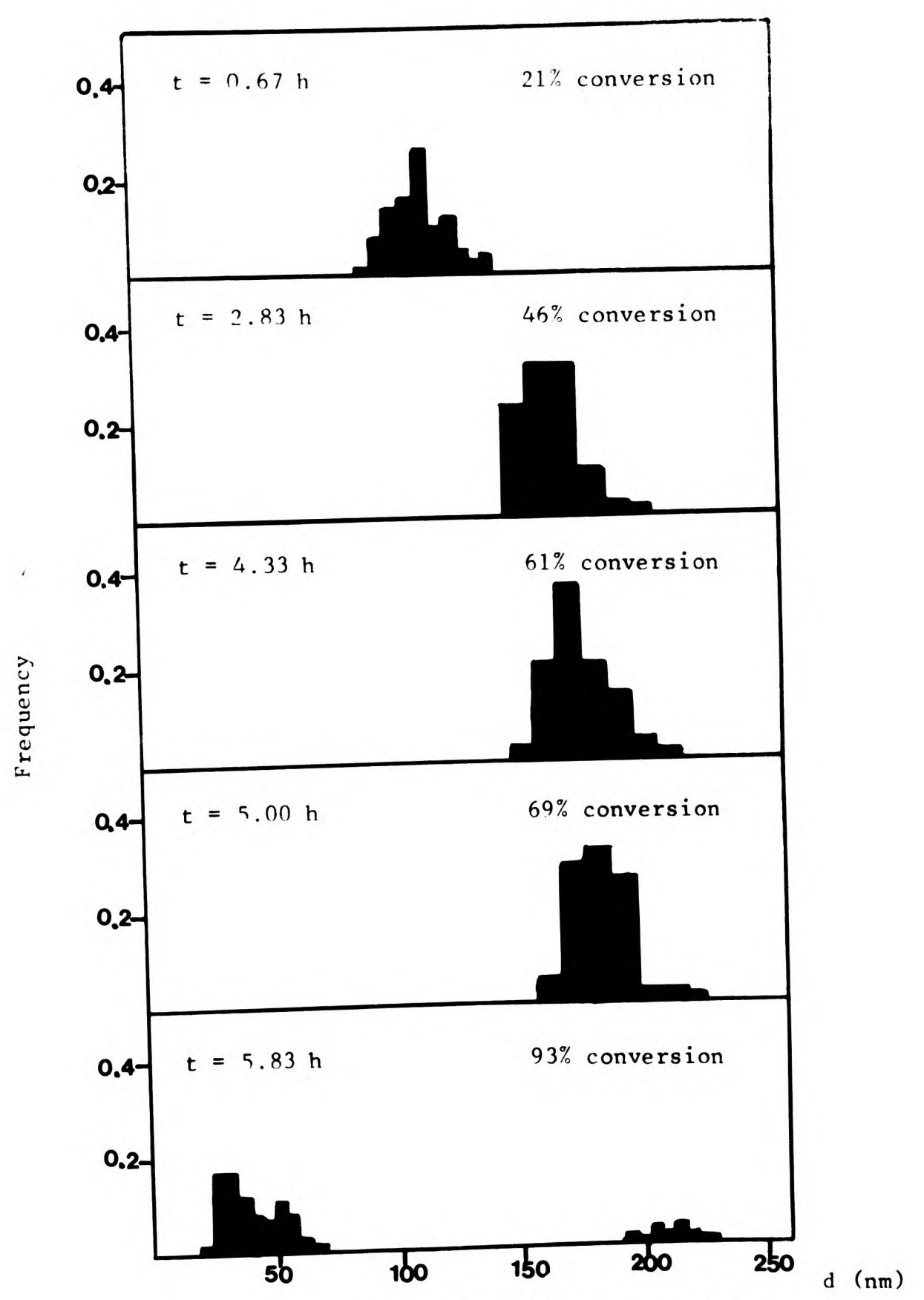

Fig. 7.15: Variation in particle diameter with time in a reaction initiated and stabilised by $FA(EO)_{24}Es$ at $60^{o}C$.

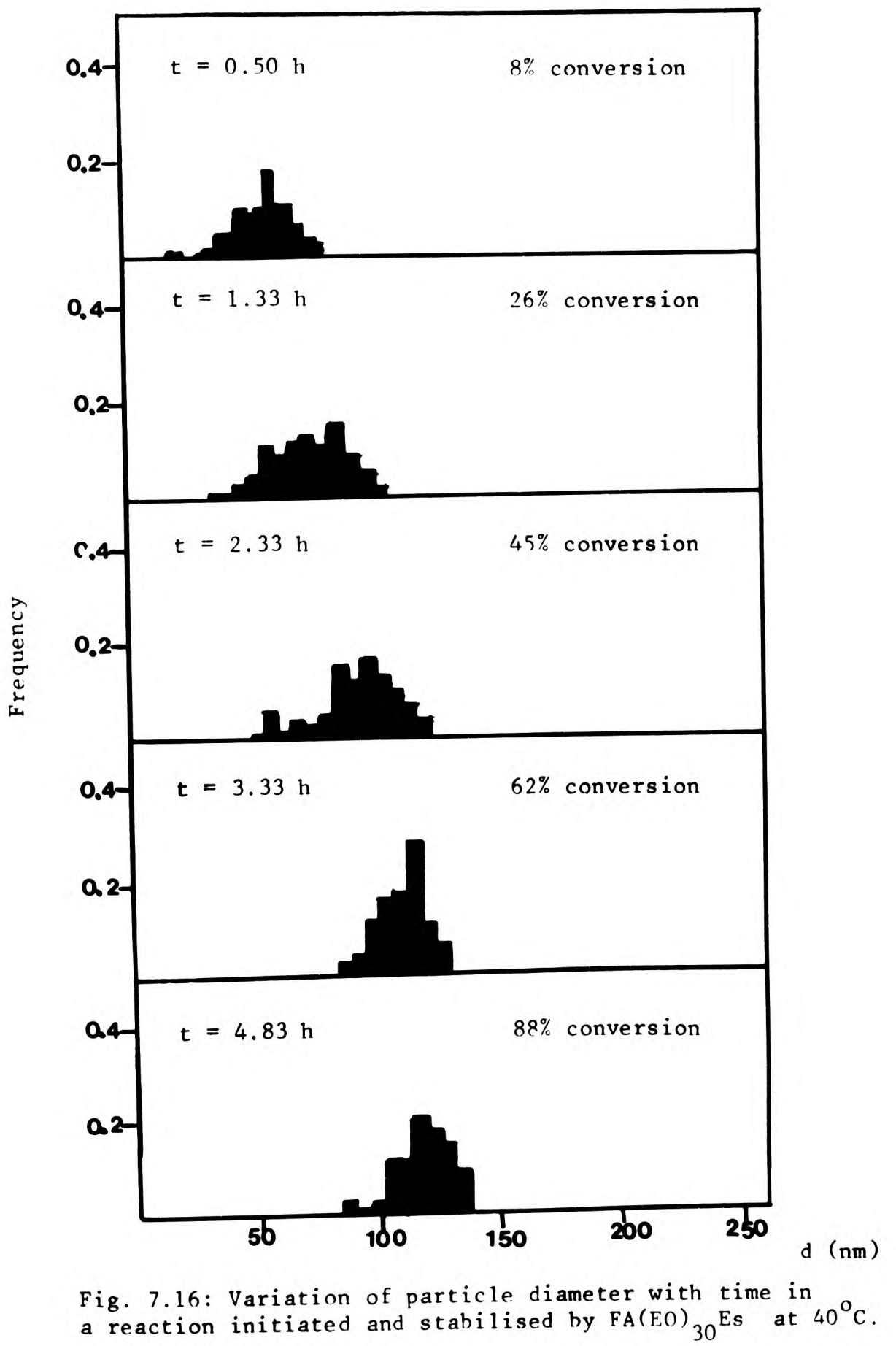

Fig. 7.16: Variation of particle diameter with time in a reaction initiated and stabilised by $FA(EO)_{30}Es$ at $40^{o}C$.

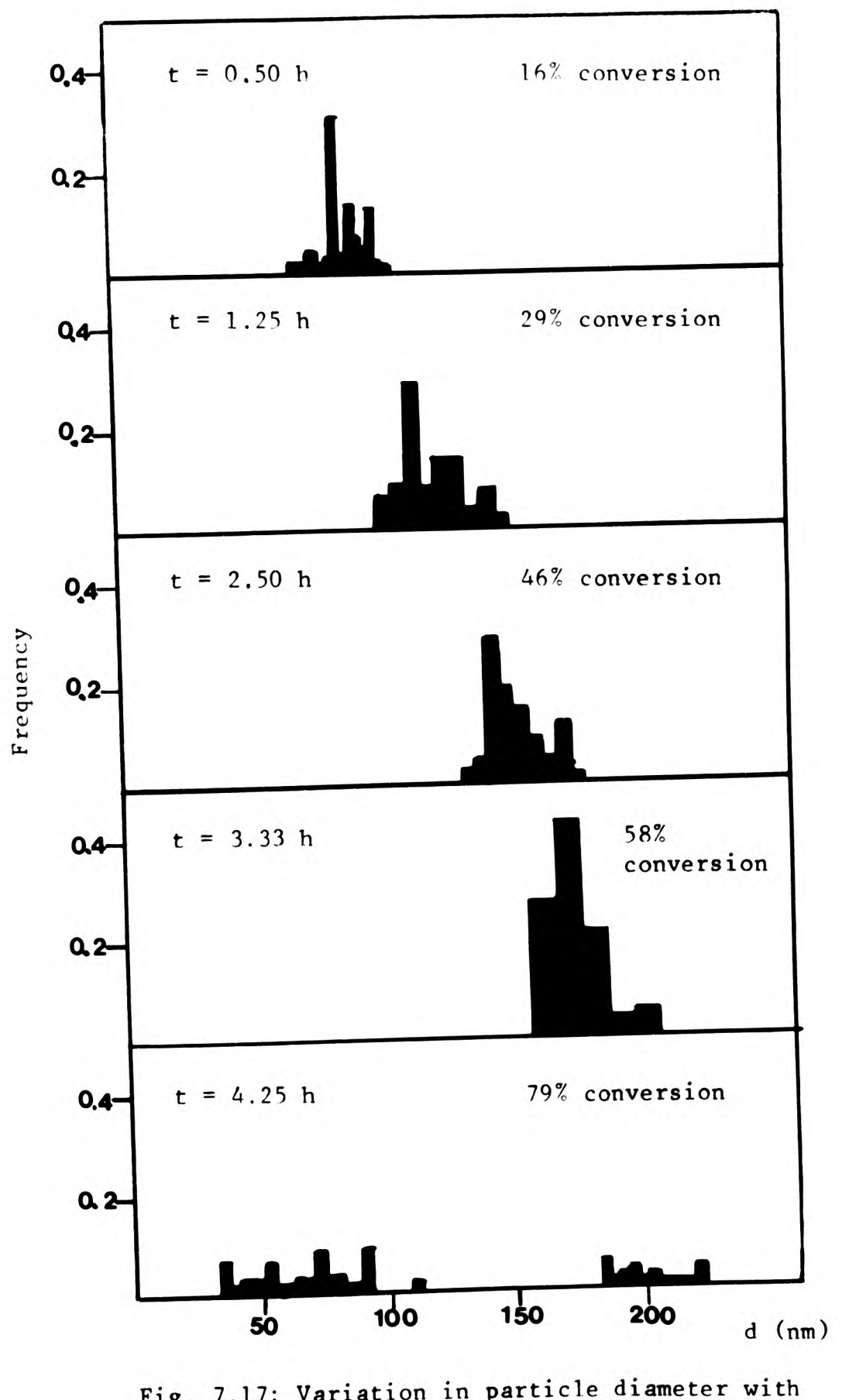

Fig. 7.17: Variation in particle diameter with time in a reaction initiated and stabilised by $FA(EO)_{30}Es$ at $60^{o}C$.

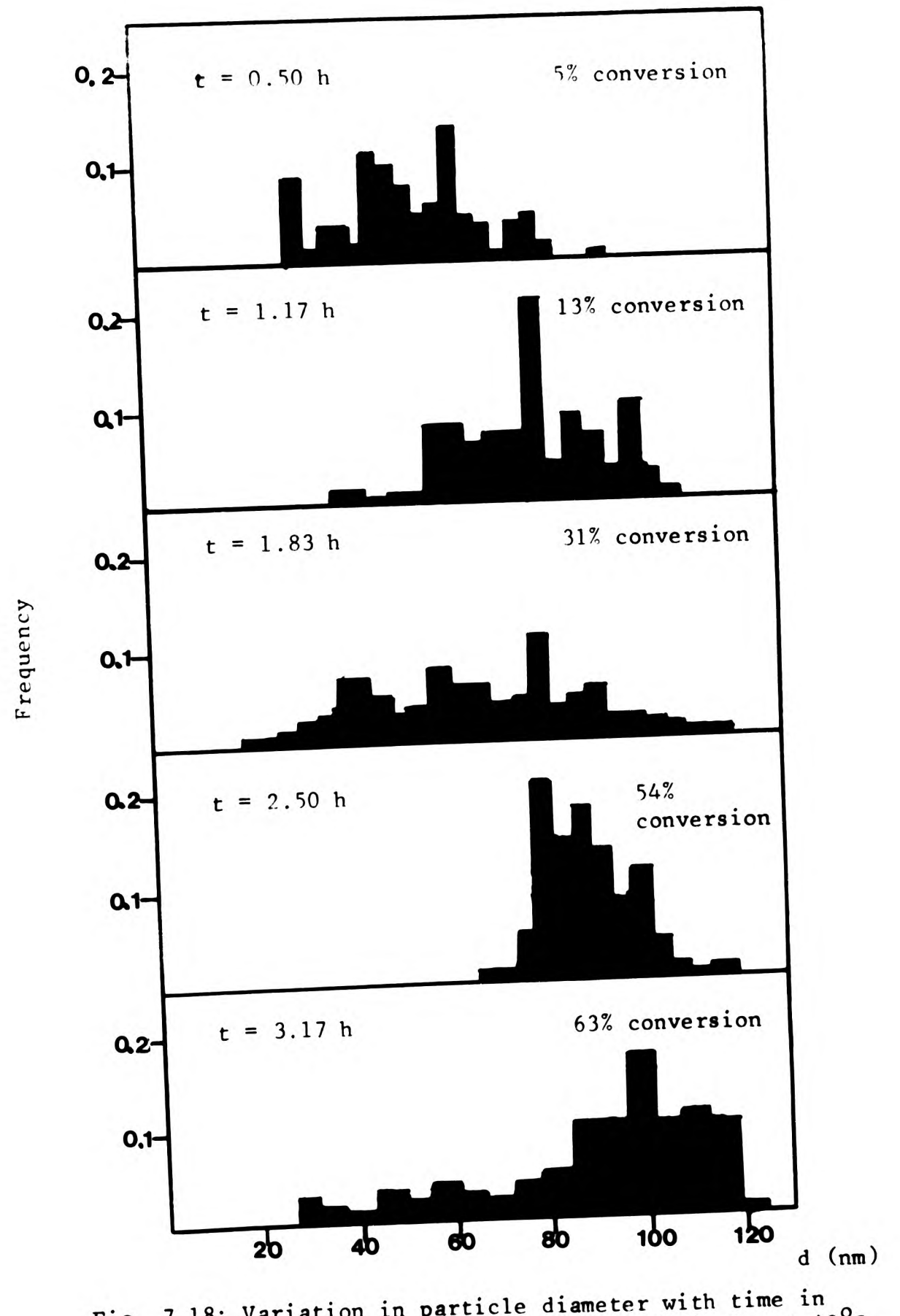

Fig. 7.18: Variation in particle diameter with time in a reaction initiated and stabilised by $FA(EO)_{60}Es$ at $40^{o}C$.

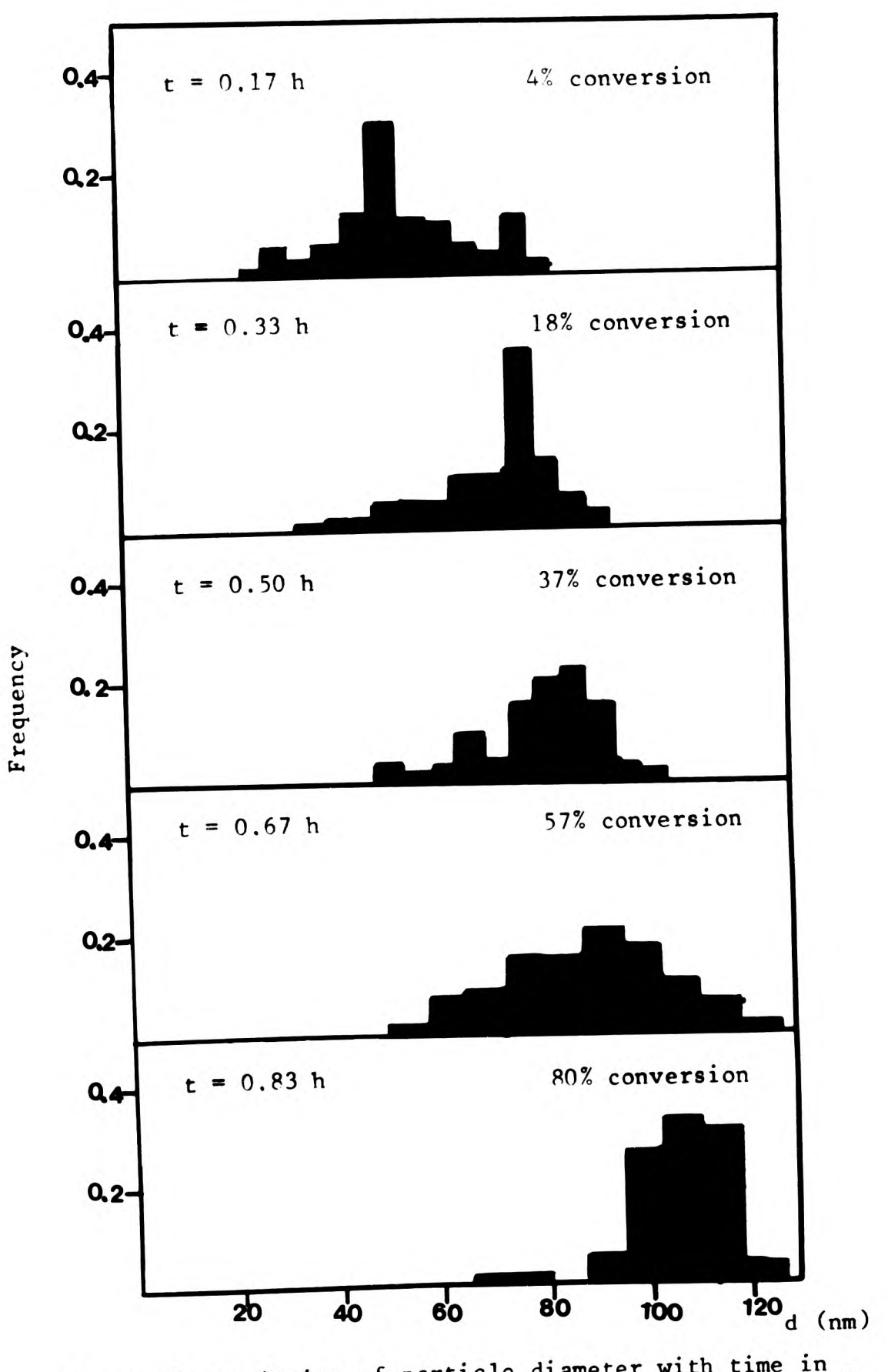

Fig. 7.19: Variation of particle diameter with time in a reaction initiated and stabilised by $FA(EO)_{60}Es$ at $60^{o}C$.

distribution for reactions initiated by $FA(EO)_{60}Es$ at 60°C, $FA(EO)_{24}Es$ at 60°C, $FA(EO)_{60}Es$ at 40°C, $FA(EO)_{30}Es$ at 40°C and $FA(EO)_{30}Es$ at 60°C are given in Figs. 7.15-7.19.

Thus, the emulsion polymerisation of styrene using $FA(EO)_{24}Es$ and $FA(EO)_{30}Es$ as initiator/stabilisers above 50°C produces a second generation of particles at a conversion of approximately 60%. The particle-size distribution becomes bimodal. The second crop of particles is smaller than the first crop. This second generation did not occur in reactions below 50°C or at any of the temperatures studied in the case of reactions initiated by $FA(EO)_{45}Es$ or $FA(EO)_{60}Es$. Also, all the results show that the final product in all cases is a stable latex produced by emulsion polymerisation, since the particle sizes of the polymer latices are well within the range typical of emulsion polymerisation. Studies of bulk polymerisation carried out using $FA(EO)_{14}Es$, $FA(EO)_{24}Es$, $FA(EO)_{30}Es$, $FA(EO)_{45}Es$ and $FA(EO)_{60}Es$ as initiators showed that hardly any polymerisation had taken place in the six hours that the reaction was allowed to proceed at 50°C. The solids content, on average, was approximately 3.2 g per 40 ml of styrene. The result was practically identically when AZBN was used as the initiator. This poor result may be due to a low initiator concentration or to the slow decomposition of the azo compound at 50°C. However, when emulsion polymerisation of styrene was carried out using the same amount of initiator and the same proportion of styrene, the solids content for the slowest of all the reactions, i.e., that initiated and stabilised by $FA(EO)_{24}Es$, was approximately 22 g per 40 ml of styrene. It seems justified to conclude that the amount of bulk polymerisation which occurred in the emulsion polymerisation systems studied was negligible. All the latices produced are stable at least over a period of months and some for over a year. Yet some of the conversion-time curves obtained for emulsion polymerisation reactions initiated and stabilised by $FA(EO)_{24}Es$ and $FA(EO)_{30}Es$ can hardly be described as being typical of emulsion polymerisation reactions. Similar results were obtained by Piirma and Chang[185] when they studied the polymerisation of styrene in the presence of a non-ionic surfactant and a persulphate initiator. The surfactant used was tridecyloxypoly(ethyleneoxy)ethanol, $C_{13}H_{27}(OC_2H_4)_{15}OH$, referred to by them by the commercial designation 'Emulphogen BC-840'. These

workers' results show two regions of constant rate of polymerisation: a lower rate of polymerisation from 5% to 30% conversion, and a much higher rate of polymerisation after 40% conversion. Piirma and Chang[185] concluded that the two regions of constant rate observed in their system can only be caused by a two-stage nucleation mechanism; that the important features in this system are the solubility of the surfactant in a monomer (ca. 40%) and the very intimate association between the surfactant, the monomer and the oligomeric species generated from the aqueous phase. As the polymerisation proceeds, the monomer droplet phase disappears, thereby causing the release of considerable numbers of surfactant molecules into the aqueous phase. The excess surfactant concentration soon reaches a critical concentration and cannot be accommodated by the existing particles. These surfactant molecules nucleate a new generation of particles.

The degree of conformity to the Smith-Ewart prediction for the emulsion polymerisation of styrene in the presence of Emulphogen BC-840 was also investigated by these workers. The initiator concentration was kept constant, but variable emulsifier concentrations were used for the purpose. Their results show that N was proportional to the 2.66 power of the concentration of BC-840, where N is the number of particles per unit volume. This deviation from Smith-Ewart behaviour is explained as being primarily due to the solubility of Emulphogen BC-840 in styrene. Because of the solubility of the surfactant in styrene, these workers propose that the number of particles in emulsion polymerisation using monomer-solubl emulsifier should follow the equation

$$N \propto [\text{emulsifier}]_{\text{effective}}$$

where "$[\text{emulsifier}]_{\text{effective}}$" denotes the total emulsifier minus the emulsifier in the monomer droplets minus the emulsifier in non-micellar form.

Piirma and Chang[185] also found that the molecular weight after the reaction had entered the second stage, like the particle size, showed a bimodal distribution, and that those particles generated at the second stage contained polymer of higher average molecular weight than that

contained in the particles generated early in the reaction.

The results obtained from the present investigation closely resemble those found by Piirma and Chang, but are not identical. This is not surprising, since important differences are to be found in the recipe used. While the initiator and stabiliser are combined in one molecule in the present work, Piirma and Chang used separate initiator and stabiliser in their work. Moreover, their initiator is water-soluble, whereas the ones used in the present investigation are soluble in styrene as well as in water. The stabiliser used by Piirma and Chang is also a conventional surfactant, while the stabilisers used in the present investigation appear to show no tendency to form micelles, although they do reduce the surface tension of water.

Emulsion polymerisation reactions initiated and stabilised by $FA(EO)_{24}Es$ and $FA(EO)_{60}Es$ resemble most closely those stabilised by Emulphogen BC-840, though there are striking differences. At the initial stages of the polymerisation, Piirma and Chang's reaction showed an initial period of constant low rate from 5% to 30% conversion, with no clear induction period, followed by a sharp rise in rate, while reactions initiated and stabilised by $FA(EO)_{24}Es$ at 50°C showed a high initial rate, either constant or slightly decreasing, followed by a period of lower but constant rate. Electron micrographs show that the number of particles varies in the first portion of the curve, but remains constant in the second, linear, portion.

Reactions initiated and stabilised by $FA(EO)_{24}Es$ and $FA(EO)_{30}Es$ above 50°C showed a high initial rate but the rate then decreased until the conversion reached approximately 20%. It was observed from the electron micrographs that initially a large number of particles formed and some coagulation took place. It is believed that some coagulation occurs because the large number of particles has a large surface area and there is not enough stabiliser in the water phase to stabilise all the particles.

At about 20% conversion the rate of polymerisation becomes constant. From this point on, reactions initiated by $FA(EO)_{24}Es$ and $FA(EO)_{30}Es$ behaved similarly to the reactions stabilised by Emulphogen BC-840 as

reported by Piirma and Chang[185]. These workers only carried out the reaction at 50°C. As was stated earlier, neither reactions initiatiated by $FA(EO)_{24}Es$ nor reactions initiated by $FA(EO)_{30}Es$ behave in his fashion at 50°C. Furthermore, below 50°C reactions initiated and stabilised by these compounds resemble conventional emulsion polymerisation reactions. Thus, it must be concluded that the change in shape of the conversion-time curves for these reactions is closely linked with temperature.

Also, Emulphogen BC-840 generates new particles at approximately 40% conversion. In this present investigation, the conversion at which the generation of new particles commences seems to depend upon the reaction temperature, as shown in Table 7.10, although it has to be borne in mind that batch-to-batch reproducibility is difficult to attain (Fig. 6.20); the shapes of the conversion-time curves are reproducible, but not the rates. The reason for the lack of reproducibility of the rates is unknown.

Temperature (°C)	% conversion at which new particles first appear	
	$FA(EO)_{24}Es$	$FA(EO)_{30}Es$
55	68	53
60	52	38
65	50	35

Table 7.10: % conversion at which a secondary crop of particles first forms, and the dependence upon temperature.

It appears that the higher the temperature is, the lower is the conversion at which the secondary crop of particles appears. With new batches of ester, the higher rate began to be observed at even higher conversions. Since the new particles are generated in some cases at 68-70% conversion (Fig. 6.20), it is difficult to envisage the disappearance of the monomer droplets as a separate phase as being the cause of the appearance of the new particles, as suggested by Piirma and Chang. Moreover, the onset of the higher rate seems to be dependent upon the polyoxyethylene chain length of the initiator/stabiliser, since the acceleration occurs at lower conversion when $FA(EO)_{30}Es$ is used as initiator/stabiliser than when

$FA(EO)_{24}Es$ is used.

The effect of temperature can be summarised for both reactions initiated by $FA(EO)_{24}Es$ and by $FA(EO)_{30}Es$ by saying that, as the temperature is raised, the acceleration in rate begins to occur at lower conversions.

One of the reasons why the Trommsdorff effect has been rejected as the cause of the acceleration, even if this acceleration occurs at around 70% conversion in some cases, is that electron micrographs show an order-of-magnitude increase in the number of particles present at this particular conversion from the constant-rate number of particles present during the earlier stages of the reaction. It is not surprising that the same effect is observed at approximately 50% conversion at 65°C for polymerisations initiated by $FA(EO)_{24}Es$ and at approximately 35% conversion for polymerisations initiated by $FA(EO)_{30}Es$ at the same temperature (Table 7.10).

For polymerisations initiated by $FA(EO)_{24}Es$ and $FA(EO)_{30}Es$ above 50°C, then, a great number of particles is generated at the onset of the reaction, but some coagulation takes place, due presumably to there being insufficient stabiliser at the particle interface to cover their great surface area. After about 20% conversion there is no more coagulation and a period of constant rate sets in. At a certain conversion, depending on temperature and polyoxyethylene chain length, new nucleation of particles occurs, giving rise to an increase in the rate of polymerisation.

It is believed that nucleation of particles, when $FA(EO)_{24}Es$ and $FA(EO)_{30}Es$ are used as initiator/stabiliser, follows the behaviour of surfactant-free emulsion polymerisation discussed by Fitch[41]; i.e., particles are formed by homogeneous nucleation. This proposal is supported by the fact that surface-tension measurements provided no evidence of micelle formation by $FA(EO)_{24}Es$ or by $FA(EO)_{30}Es$ in water, and by the fact that results for the number of particles generated show comparable trends to those for Fitch's surfactant-free systems for the first nucleation stage (Fig. 7.20). However, reactions initiated by $FA(EO)_{45}Es$ and $FA(EO)_{60}Es$ do not seem to follow the same pattern of nucleation as that followed by reactions initiated by $FA(EO)_{24}Es$ and

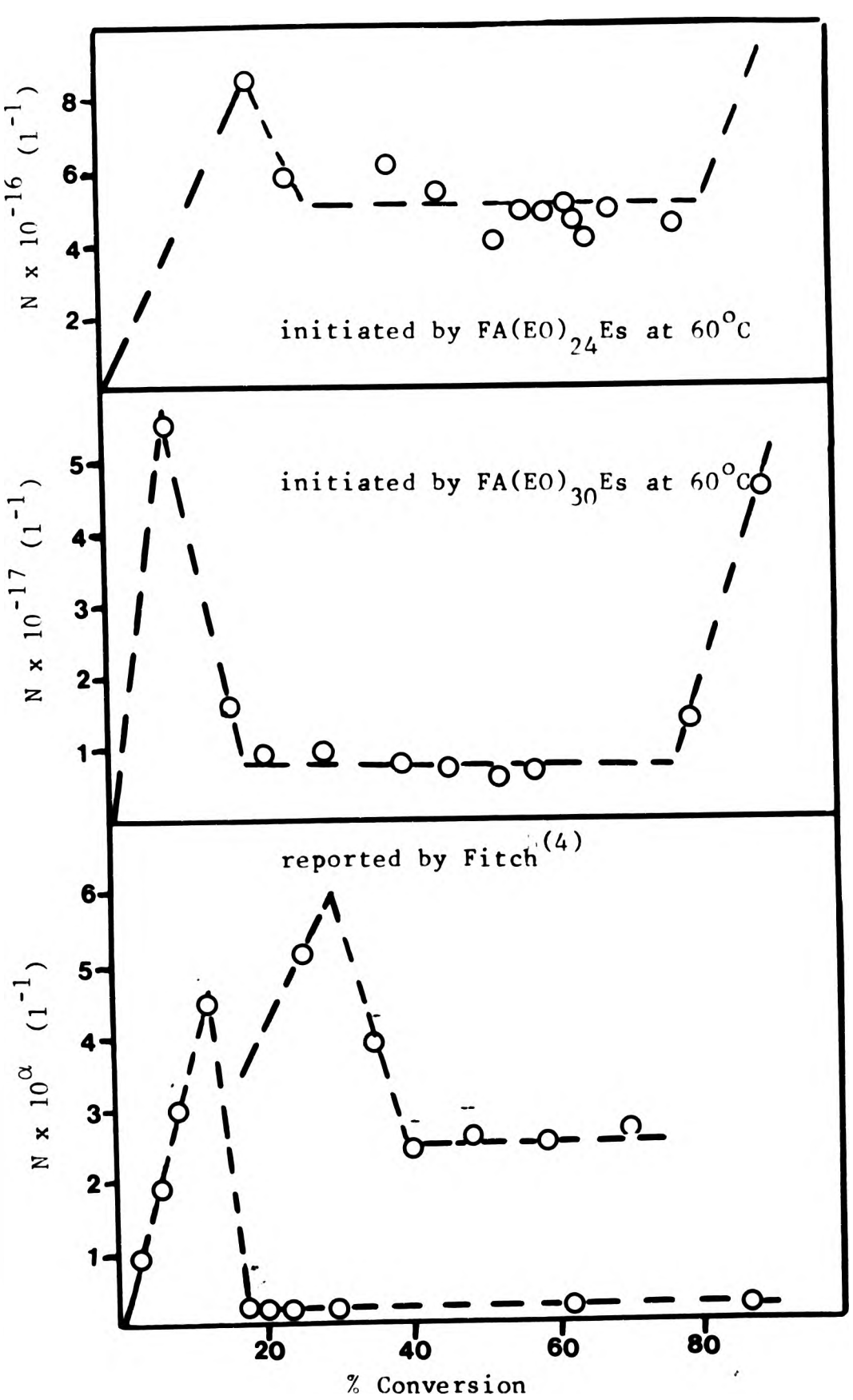

Fig. 7.20: Variation in number of particles with conversion.

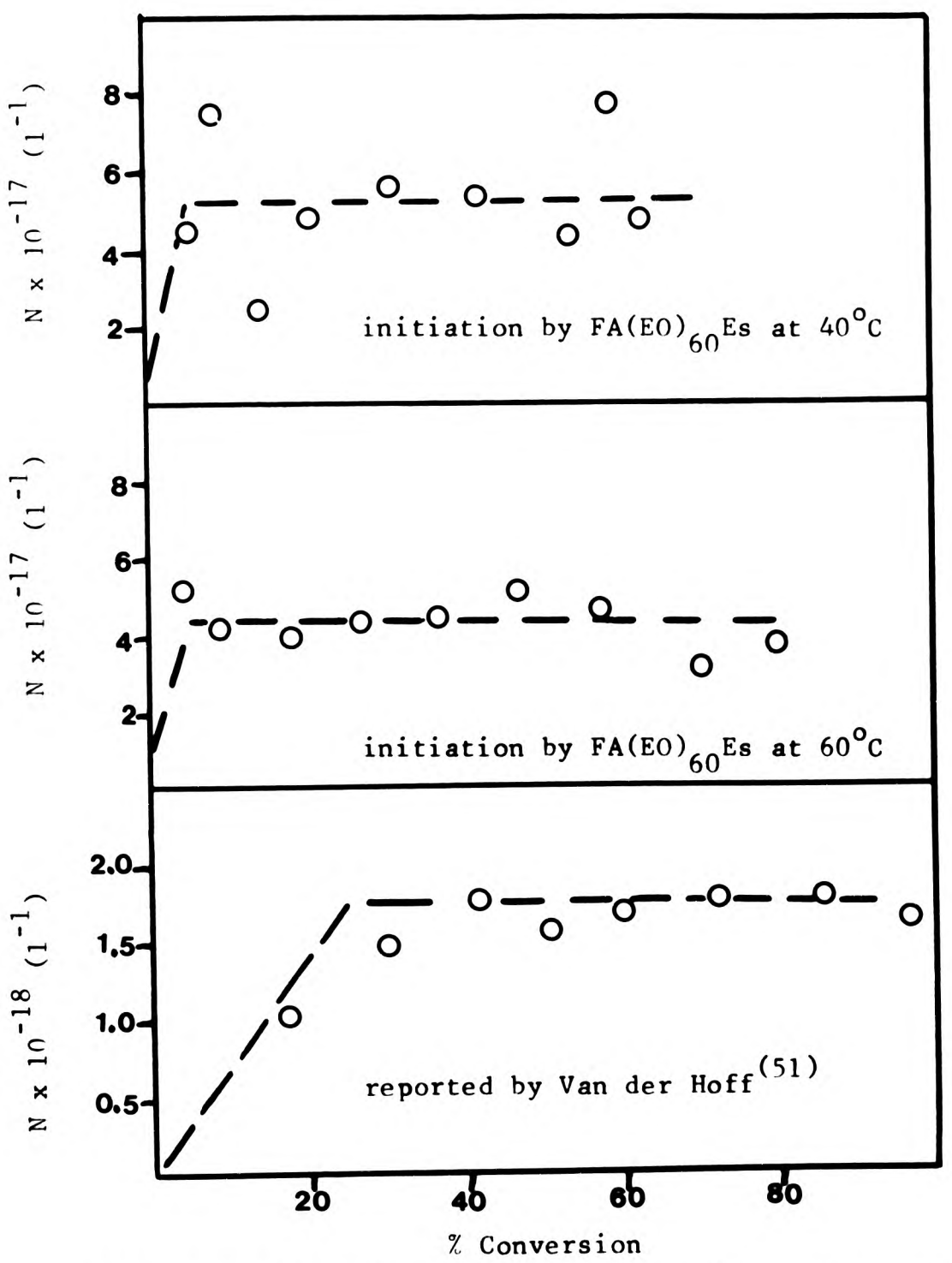

Fig. 7.21: Variation in number of particles with conversion.

$FA(EO)_{30}Es$. The former seem closer to a micellar nucleation mechanism (Fig. 7.21). Unfortunately the findings are not conclusive, and perhaps homogeneous nucleation as well as micellar nucleation takes place when $FA(EO)_{45}Es$ and $FA(EO)_{60}Es$ are used as emulsion initiator/stabilisers.

In order to understand the behaviour of the emulsion polymerisation of styrene in the presence of $FA(EO)_{24}Es$ and $FA(EO)_{30}Es$, and to a lesser extent in the presence of $FA(EO)_{45}Es$ and $FA(EO)_{60}Es$, as initiator/stabilisers, one important feature to be considered is the solubility of these compounds in styrene. The partition coefficient of these compounds between styrene and water could not be investigated directly, but the possibility of close association between the initiator/stabiliser, the monomer, the oligomeric species generated from the aqueous phase, and the aqueous phase itself cannot be ignored. The solubility in styrene would be expected to be greatest for $FA(EO)_{24}Es$ and lowest for $FA(EO)_{60}Es$, because the hydrophilic portion is shortest for the former and largest for the latter.

It has been observed that, as the concentration of the ester is increased, the shape of the conversion-time curve changes from that resembling bulk polymerisation at low concentrations to that typical of conventional emulsion polymerisation at high ester concentrations. At low concentrations, the amount of ester dissolved in the water phase is inadequate to promote typical emulsion polymerisation reactions and the result is closer to that observed in bulk reactions. As the ester concentration is increased, more of the compound is available to dissolve in the water phase and typical emulsion polymerisation behaviour is observed, the amount of bulk polymerisation being negligible since emulsion reactions are so much faster.

The study of the effect of temperature upon the shapes of the conversion-time curves and upon the rate of polymerisation reactions reveals that at temperatures below 50°C, conventional emulsion polymerisation curves are obtained and the polymerisation rate decreases with decreasing temperature. Above 50°C, two regions of constant rate are observed. At 50°C, the curves are a mixture of the two types. In general, it is obseved that, as the temperature increases, the rate increases up to 50°C;

however, as the temperature is raised further, the rate of polymerisation decreases. Moreover, a general decrease in the number of particles is observed as the temperature increases, which will account for the decrease in the rate. These particle numbers were calculated form data obtained from the Coulter Nanosizer and therefore do not show the secondary particle nucleation. Thus the number of particles is that appropiate to the lower rate (I) in all cases, and therefore valid to include here. From the results one can perhaps infer that the partition coefficient between the water and styrene phases of $FA(EO)_{24}Es$ and $FA(EO)_{30}Es$ is, not surprisingly, temperature-dependent. At lower temperatures, the esters are more soluble in the water phase and typical emulsion polymerisation behaviour is observed. Above 50°C the solubility of the ester in the water phase decreases with increasing temperature, and at 50°C the behaviour is intermediate between the two models given above. This interpretation is supported by the fact that both the fatty-alcohol ethoxylate and the esters derived from them show the inverse solubility phenomenon.

When studying the effect of increasing the volume of water on the rate of polymerisation, it is observed that the rates for the reactions initiated by $FA(EO)_{24}Es$ and $FA(EO)_{30}Es$ are dependent on the phase ratio. The rate of polymerisation increases as the total volume of water increases. It seems reasonable to assume that the total amount of ester dissolved in the water phase increases with increasing volume of water and thus that the total number of particles formed increases also. This is indeed observed for reactions initiated by $FA(EO)_{24}Es$, but reactions initiated by $FA(EO)_{30}Es$ show no appreciable change in the number of particles. It has to be borne in mind that the increase in rate with increasing volume of water is more pronounced for reactions initiated by $FA(EO)_{24}Es$ than for reactions initiated for $FA(EO)_{30}Es$, and since the particle diameters were measured with the Coulter Nanosizer, the inability of this instrument to register small particles may be the reason for the discrepancy.

The polymerisation reactions of styrene initiated and stabilised by $FA(EO)_{45}Es$ and $FA(EO)_{60}Es$ under the conditions studied behaved in general as conventional emulsion polymerisations. As the concentration of ester was increased, so the rate increased. Not surprisingly, the

number of particles also increased. The rate of polymerisation increased with incresing temperature, but the reaction initiated by $FA(EO)_{45}Es$ showed a decrease in rate at high temperatures. Reactions initiated both by $FA(EO)_{45}Es$ and by $FA(EO)_{60}Es$ showed an increase in the number of particles formed as the temperature increased, but a decrease when high temperatures were reached (ca. 65°C) (Fig. 7.10). The reason for this behaviour is probably that, although $FA(EO)_{45}Es$ and $FA(EO)_{60}Es$ are so much more soluble in the water phase than are $FA(EO)_{24}Es$ and $FA(EO)_{30}Es$, at high temperatures they begin to show the properties exhibited by $FA(EO9_{24}Es$ and $FA(EO)_{30}Es$; i.e., they begin to be more soluble in the oil phase and thus a smaller number of particles is formed and consequently the rate of polymerisation drops.

The effect of increasing the volume of water showed that the rates of polymerisation reactions initiated by $FA(EO)_{45}Es$ and $FA(EO)_{60}Es$ at 45°C are practically independent of the total volume of water in the range studied. The number of particles formed for the $FA(EO)_{60}Es$ showed again the independence of volume of water. However, the reaction initiated by $FA(EO)_{45}Es$ showed a great increase in the number of particles as the water volume increased. This result is questionable, since the increase in number of particles is greater than for reactions initiated and stabilised by $FA(EO)_{24}Es$ and $FA(EO)_{30}Es$ under the same conditions.

It is more difficult to draw conclusions from the results for the dependence of rate per particle upon temperature. These difficulties arise from the fact that the polymerisations carried out in the presence of $FA(EO)_{24}Es$ and $FA(EO)_{30}Es$ gave conversion-time curves whose shape changed with changing temperature. When plotting the relevant graphs, the rates used have always been the rates obtained from the linear portion of the curve where the number of particles is constant according to electron microscopic measurements. One would expect to find that the rate per particle increases as the temperature is raised, because k_p increases and thus the rate of polymerisation also increases. Unfortunately, no inferences can be drawn for the polymerisations initiated by $FA(EO)_{24}Es$. Those reactions in which $FA(EO)_{30}Es$ was used as initiator/stabiliser seem to show an increase in the rate of

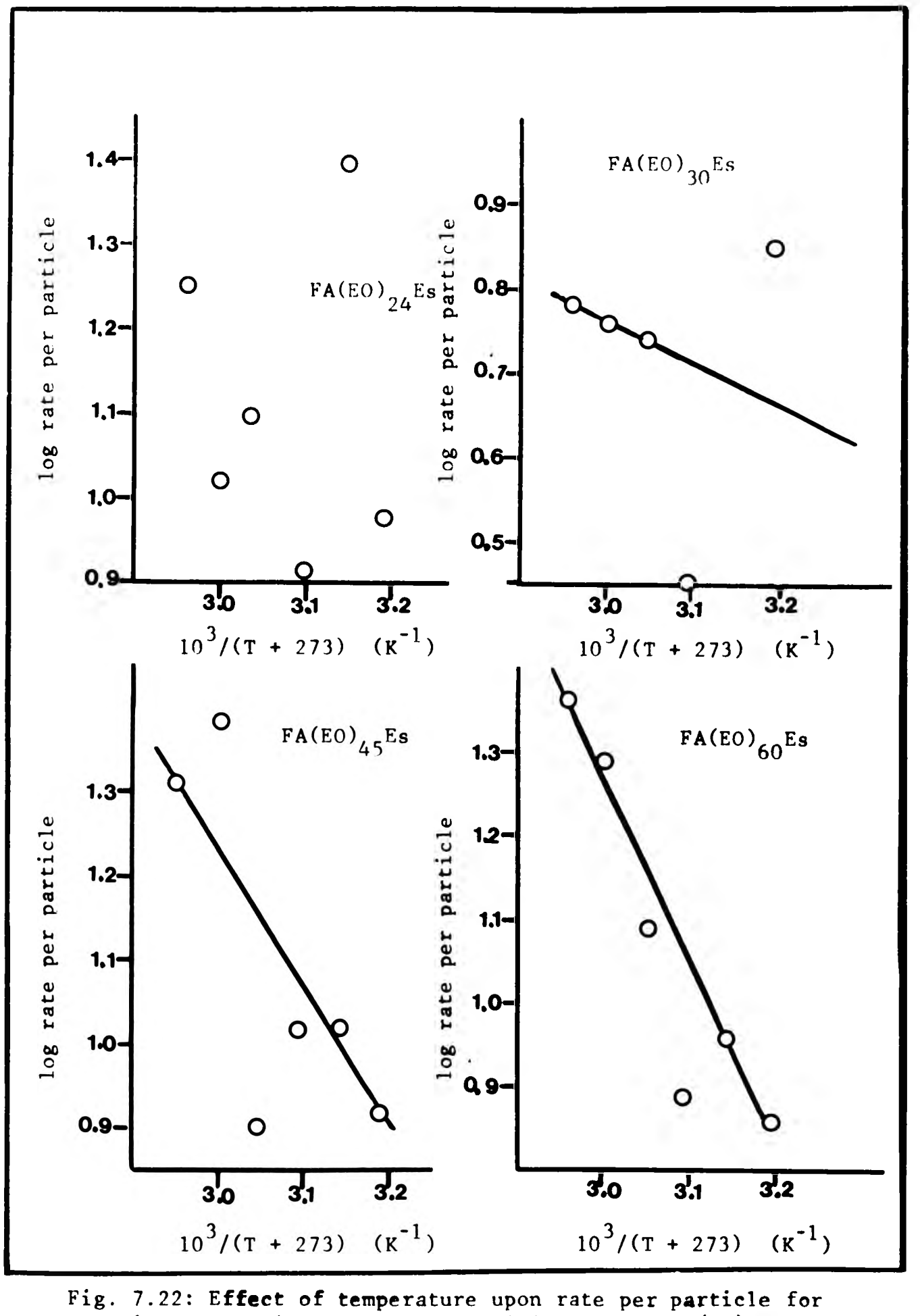

Fig. 7.22: Effect of temperature upon rate per particle for emulsion polymerisation reactions initiated by $FA(EO)_{24}Es$, $FA(EO)_{30}Es$, $FA(EO)_{45}Es$ and $FA(EO)_{60}Es$.

polymerisation with increasing temperature, where the rates are derived from curves of similar shapes. When $FA(FO)_{45}Fs$ and $FA(FO)_{60}Fs$ were used as initiator/stabilisers, the results seemed to agree with expectation; i.e., the rate per particle increases with increasing temperature.

An estimation of the average number of radicals per particle, n, was made using the following formula:

$$dM/dt = nk_p[M]N$$

where [dM/dt]/N is the rate per particle. The effect of temperature upon rate per particle for emulsion polymerisation reactions initiated by $FA(FO)_{24}Fs$, $FA(FO)_{30}Fs$, $FA(FO)_{45}Fs$ and $FA(FO)_{60}Fs$ are given in Fig. 7.22.

The average number of radicals per particle was found using two different values for k_p and for [M]. Calculation I involved the use of values of k_p and [M] at 50°C from the work carried out by Gilbert and Napper[198]. Calculation II used values from Van der Hoff[51] and the Polymer Handbook[197].

Since k_p and [M] vary with temperature, values of k_p for the required temperatures were obtained from a plot of log k_p versus 1/T given in the Polymer Handbook, and values of [M] at a given temperature were found from a plot of [M] versus T given by Van der Hoff[51]. The values used in the calculations of average number of radicals per particle are given in Table 7.11.

T (°C)	k_{p1} (l mol^{-1} s^{-1})	k_{p2} (l mol^{-1} s^{-1})	$[M]_1[M]_2$ (mol l^{-1})	(mol l^{-1})
40	183	106	6.07	5.47
45	218	139	5.89	5.39
50	258	179	5.80	5.30
60	357	293	5.63	5.13

Table 7.11: Values of k_p and [M] used in calculating the average number of radicals per particle.

The results obtained are summarised in Table 7.12.

T (°C)	$\underline{FA(FO)_{24}Fs}$	$\underline{FA(FO)_{30}Fs}$	$\underline{FA(FO)_{45}Fs}$	$\underline{FA(FO)_{60}Fs}$
40	---	0.34[b]	---	0.26[b]
45	0.49[a]	0.49[a]	---	---
50	0.42[a]	0.43[a]	0.46[a]	0.48[a]
60	0.48[b]	0.39[b]	---	0.60[b]

Mean average number of radicals per particle: 0.44

a: calculated by averaging the rate per particle obtained at different initiator/stabiliser concentrations

b: calculated by dividing a single rate by the average particle number at different times

Table 7.12a: Average number of radicals per particle using calculation I ($\underline{k_{p1}}$ and $\underline{[M]_1}$).

T (°C)	$\underline{FA(FO)_{24}Fs}$	$\underline{FA(FO)_{30}Fs}$	$\underline{FA(FO)_{45}Fs}$	$\underline{FA(FO)_{60}Fs}$
40	---	0.65[b]	---	0.50[b]
45	0.84[a]	0.83[a]	---	---
50	0.66[a]	0.67[a]	0.73[a]	0.74[a]
60	0.65[b]	0.52[b]	---	0.81[b]

Mean average number of radicals per particle: 0.69

a and b have the same significance as in Table 7.12a.

Table 7.12b: Average number of radicals per particle using calculation $\underline{II}$ (k_{p2} and $[M]_2$).

The mean average number of radicals per particle found for the systems studied is close to 0.5. This is, of course, the average number of radicals per particle that Smith and Ewart predicted for their Case 2 model of emulsion polymerisation reactions.

It is now necessary to consider whether the average number of radicals per particle is close to 0.5 because the reaction conforms to the Smith-Ewart Case 2 model. The azo esters used as initiator/stabilisers for the emulsion polymerisation of styrene are soluble in the oil phase and also in the water phase. Furthermore, these compounds act as stabilisers. From

the above it can be concluded that in principle there are four centres of initiation:

(i) the water phase,

(ii) the monomer droplets,

(iii) the growing polymer particles,

(iv) the surface of the polymer particles.

The azo group can decompose in the water phase, where the free radicals formed would grow into oligomers which would collapse into a growing particle when the required length had been attained. Monomer would be trapped inside the particle in which some ester would be dissolved, and more monomer and ester would diffuse as the monomer in the particle was consumed. Thus other initiation centres could be located inside the growing polymer particle, as well as some in the monomer droplets, but bulk polymerisation can be considered negligible from the results obtained from bulk polymerisation experiments when the esters were used as initiators. Finally, adsorbed ester molecules presumably surround the growing particles, thereby aiding stabilisation; thus initiation at the surface of the growing particle, i.e., at the water-oil interface is another possibility. Medvedev and his collaborators[24] have proposed a theory of emulsion polymerisation for many years which treats the reaction as a pseudo-homogeneous reaction in the surface layer. The equations deduced have been experimentally verified over a wide range of emulsifier and initiator concentrations for both water-soluble and oil-soluble initiators. Yet, the results obtained in the present investigation show that the average number of radicals per particle is close to 0.5. Also, very-high-molecular-weight polymers were obtained, which suggests that the average lifetime of an effective radical is long. The presence of more than one radical close by at any given time would result in rapid termination and the formation of polymers of low molecular weight; and even though low-molecular-weight compounds appear at similar elution volumes to toluene, it is believed that they are caused by impurities. The average molecular weights obtained are very high, being in some cases of the order of 10^7. The accurate measurement of molecular weights for these polystyrenes was not possible because of lack of appropriate measurement equipment in our laboratories and at RAPRA.

With the possibility that radicals are generated simultaneously at four different possible centres, how can it be explained that the average number of radicals per particle found is only 0.5?

The decomposition of the azo ester in the monomer droplets would be of little consequence, since hardly any polymer is formed in bulk for the period of the reaction.

The molecules which are decomposing within a growing polymer particle, because of the close proximity of the radicals, can easily recombine, with the net result of only the production of nitrogen. Al-Shahib and Dunn[159] have shown that, in the case of emulsion polymerisations initiated by AZBN, radicals are generated in pairs in the oil phase, but a radical escapes to the aqueous phase, leaving an isolated radical in the oil phase to initiate emulsion polymerisation. AZBN is a comparatively small molecule, and the escape of a radical derived from it into the aqueous phase may therefore seem not entirely implausible; the fatty-alcohol ethoxylate esters used in the present study are, in contrast, so large that rapid recombination of radicals seems more likely than the rapid escape of one radical from the polymer particle. Moreover, if the mechanism proposed by Al-Shahib and Dunn were operating in this case, one would expect a rather broad distribution of molecular weights, with a large proportion of low-molecular-weight polymer, since the probability of both radicals remaining in the polymer particle would be expected to be significantly greater than zero. But, as was reported in Chapter Six, the molecular weights of the polymers prepared in the present study are very high, with little sign of a broad distribution of molecular weights; consequently, the results of the present investigation do not appear to be readily consistent with a mechanism in which pairs of radicals are produced within the polymer particle. A more detailed comparison of the results of this study with the results of Al-Shahib and Dunn appears to be ruled out by the differences in concentration and particle number in the two investigations.

If we envisage the decomposition of the azo group in the water phase and the formation of growing particles by homogeneous nucleation, then the particle so far contains only one growing chain. The surface of the

growing polymer particle is surrounded by the ester acting as a stabiliser. Of those molecules decomposing into two radicals at the surface, one radical of each pair may on average diffuse into the water phase whilst the other radical enters the particle from the surface to terminate the growing chain, although in individual cases, of course, both may diffuse into the water phase or both may enter the particle. After a while, another molecule decomposes on the surface and the procedure is repeated, but this time the radical entering the particle from the surface starts the growth of another chain; and thus an average number of radicals of 0.5 per particle seems to be a reasonable possibility.

An attempt was made to estimate the efficiency of initiation of these azo compounds. The efficiency of initiation was calculated using the following formula:

$$\% \text{ efficiency} = \frac{R_i}{R_d} \times 100$$

where R_i is the rate of initiation of polymer chains, calculated as $2R_p/D_p$. R_p is the rate of polymerisation and D_p is the degree of polymerisation calculated as M_n/M_w, where M_n is the number-average molecular weight of the polymer and M_w is the molecular weight of the monomer. The assumption involved in calculating R_i is that the termination is purely by combination of two radicals and transfer is absent.

R_d is the rate of formation of primary radicals, calculated as $2k_d[I]$, where k_d is the rate coefficient for decomposition of the initiator and [I] is the concentration of initiator. A summary of the results obtained is given in Table 7.13.

Sample	Mass (g)	R_i (molecules l^{-1} s^{-1})	R_d (radicals l^{-1} s^{-1})	% efficiency
$FA(F.O)_{24}F.s$	3.0	6.25×10^{15}	7.80×10^{15}	80
$FA(F.O)_{24}F.s$	5.5	9.66×10^{16}	2.95×10^{16}	327
$FA(F.O)_{30}F.s$	3.0	2.70×10^{16}	1.42×10^{16}	190
$FA(F.O)_{30}F.s$	3.6	9.57×10^{15}	1.70×10^{16}	56
$FA(F.O)_{45}F.s$	4.0	4.57×10^{16}	3.38×10^{16}	135
$FA(F.O)_{60}F.s$	3.0	8.58×10^{16}	2.06×10^{16}	416
$FA(F.O)_{60}F.s$	6.4	3.86×10^{16}	2.14×10^{16}	180

Table 7.13a: Rates of initiation and of radical formation and efficiencies of initiation using different masses of ester at 50°C.

Sample	Temp. (°C)	R_i (molecules l^{-1} s^{-1})	R_d (radicals l^{-1} s^{-1})	% efficiency
$FA(F.O)_{24}F.s$	40	5.39×10^{15}	7.79×10^{15}	69
$FA(F.O)_{24}F.s$	50	6.25×10^{15}	7.80×10^{15}	80
$FA(F.O)_{30}F.s$	50	9.57×10^{15}	1.70×10^{16}	56
$FA(F.O)_{45}F.s$	40	3.76×10^{16}	8.68×10^{15}	433
$FA(F.O)_{45}F.s$	60	7.61×10^{16}	9.93×10^{16}	77
$FA(F.O)_{60}F.s$	50	3.86×10^{16}	2.14×10^{16}	180
$FA(F.O)_{60}F.s$	60	4.49×10^{17}	7.09×10^{16}	633

Table 7.13b: Rates of initiation and of radical formation and efficiencies of initiation using a constant amount of ester at different temperatures.

Unfortunately, since some of the efficiences are well over 100%, it has to be concluded that either (1) there is a great deal of error involved in the calculation of the efficiencies, since the average molecular weight used in the calculations may perhaps be questioned, or (2) the assumptions involved in the calculations of efficiencies are not correct in this

particular case. One such assumption is the absence of transfer of radicals from the polymerisation centres.

Unfortunately, the results show a great deal of variation and there is no obvious trend in the calculated efficiencies with respect to either the concentration of the initiator/stabiliser or the temperature of polymerisation.

One way of accounting for the very high efficiencies calculated would be to postulate the occurrence of a substantial degree of transfer of radicals from the polymerising centres to other centres, but such a high degree of transfer would reduce the molecular weight of the product and does not appear to be consistent with the high molecular weights obtained.

The percentage of undecomposed initiator at the end of certain reactions using $FA(EO)_{24}Es$, $FA(EO)_{30}$, $FA(EO)_{45}$ and $FA(EO)_{60}Es$ as initiator/stabilisers at different temperatures has been calculated from the equation

$$m_t/m_0 = 2^{-(t/t_{\frac{1}{2}})}$$

where m_t is the mass of initiator remaining at time t, m_0 is the initial mass of initiator and $t_{\frac{1}{2}}$ is the half-life of the initiators. The results are given in Table 7.14.

Initiator	T (°C)	t (h)	$t_{\frac{1}{2}}$ (h)	% Initiator undecomposed	% Conversion
$FA(EO)_{24}Es$	40	4.0	241	99%	50%
$FA(EO)_{24}Es$	50	3.0	111	98%	70%
$FA(EO)_{24}Es$	60	7.5	18.5	76%	80%
$FA(EO)_{30}Es$	50	3.0	109	98%	73%
$FA(EO)_{30}Es$	60	6.5	18.9	79%	68%
$FA(EO)_{30}Es$	65	6.5	10.6	65%	90%
$FA(EO)_{45}Es$	50	2.2	59.4	97%	75%
$FA(EO)_{45}Es$	60	1.5	18.9	95%	90%
$FA(EO)_{45}Es$	65	0.8	10.7	95%	60%
$FA(EO)_{60}Es$	50	2.0	87.5	98%	80%
$FA(EO)_{60}Es$	60	0.8	26.4	98%	73%
$FA(EO)_{60}Es$	65	0.8	10.0	97%	79%

Table 7.14: % Undecomposed initiator at the end of the reaction when $FA(EO)_{24}$, $FA(EO)_{30}Es$, $FA(EO)_{45}Es$ and $FA(EO)_{60}Es$ were used as initiator/stabilisers at different temperatures.

Another interesting observation is that the period of constant rate extends up to 85-90% conversion in some cases, and rarely falls short of about 75% conversion. The monomer concentration is necessarily decreasing. Therefore an opposing factor must be invoked to explain the above results. One possibility is the Trommsdorff effect. Since the viscosity increases, the probability of two radicals meeting diminishes, and thus k_t decreases. This would increase the polymerisation rate and the molecular weight. A second possibility is the formation of new particles at high polymer conversions. There is no need for a large increase in the number of polymer particles to keep the rate constant.

Concerning the order of reaction with respect to the concentration of iniiator/stabiliser, this ranges from 2.05 for $FA(EO)_{24}Es$ to 0.80 for $FA(EO)_{60}Es$. The order of reaction comes closer to one as the hydrophilic character of the ester increases. The value that Piirma and Chang found for their Emulphogen BC-840 at 50°C was 2.66 with respect to surfactant concentration only. If one bears in mind that $FA(EO)_{24}Es$ contains in its molecular structure an average of 24 oxyethylene units and that Emulphogen BC-840 has only 15 oxyethylene units, the present results seem to show considerable agreement with Piirma and Chang's. From the results, one is tempted to predict that the $FA(EO)_{14}Es$ would have an even higher order of reaction with respect to concentration of ester. It seems reasonable to conclude that the order of reaction with respect to concentration of ester is related to the number of oxyethylene units, i.e., to the hydrophilic portion. The dependence is greatest for the lowest polyoxyethylene content and lowest for the greatest content of polyoxyethylene.

Piirma and Chang maintain that, as polymerisation proceeds, the monomer droplets disappear from the aqueous phase, thereby causing the release of a considerable number of surfactant molecules. The excess surfactant concentration soon reaches a critical value and cannot be accommodated by the existing particles, thus these surfactant molecules nucleate a new generation of particles.

The results from the experiments carried out in this research project do not seem to support Piirma and Chang's claim, since a new crop of

particles does not necessarily appear at ca. 40% conversion, when the monomer droplets are believed to disappear as a separate phase, but may appear at 55-70% conversion, depending upon the temperature of the reaction as well as upon the polyoxyethylene chain length of the initiator/stabiliser. The reactions initiated by $FA(EO)_{30}Es$ accelerate at lower conversions than do reactions initiated by $FA(EO)_{24}Es$. It is believed that the reason for a secondary crop of particles is the insolubility of the ester in the growing polystyrene particle because of the change in the polymer/monomer ratio in the particles, which reduces the solubility of the ester. As the polymer particle grows, the solubility of the ester decreases until a critical point is reached at which it becomes insoluble and is expelled from the growing particles and redissolves in the water phase. Since the ester is also soluble in the monomer, presumably some monomer will come out of the growing polymer particles with the ester and will form new nucleation centres.

The fact that reactions initiated by $FA(EO)_{30}Es$ nucleate new particles at lower conversions than do reactions initiated by $FA(EO)_{24}Es$ can be explained by the fact that $FA(EO)_{24}Es$ is less soluble in water and more soluble in the monomer, and thus a greater concentration of polystyrene in the particles is required before $FA(EO)_{24}Es$ becomes insoluble and has to leave the particle. This proposal cannot explain why reaction systems which contain Emulphogen BC-840 generate new particles at 40% conversion.

CHAPTER EIGHT

SUMMARY OF CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK

8.1. Summary of conclusions drawn from the use of esters prepared from acid chloride I as initiator/stabilisers for emulsion polymerisation reactions. It was reported in Chapter Five that 4,4'-AB-4-CPA reacts with phosphorus pentachloride at room temperature to give two supposed diacid chlorides, each of which can react with two mol of straight-chain aliphatic alcohol to yield two supposed diesters. The esters are labelled 'esters A' and 'esters B'. Esters A are derived from acid chloride I and a straight-chain alcohol, and have the characteristic smell of an ester. Surprisingly, they are partially soluble in water. Esters B are derived from acid chloride II and lack the characteristic smell of esters. However, the infrared spectrum of an ester B is identical to that of the corresponding ester A. Esters B are, as expected, insoluble in water. Due presumably to the partial solubility of esters A in water, amongst other things, these compounds not only act as initiators for emulsion polymerisation but also help to stabilise a very monodisperse polystyrene latex produced in the absence of added conventional surfactant. Stable latices were obtained when using the nonyl, decyl, undecyl and hexadecyl esters A derived from 4,4'-AB-4-CPA and the appropriate straight-chain aliphatic alcohols. Unfortunately, esters B do not yield latices nor indeed do they appear to initiate any other kinds of polymerisation when used as initiator/stabilisers for the emulsion polymerisation of styrene in the absence of added conventional surfactant.

Not very surprisingly, the potassium salts of the esters A derived from 4,4'-AB-4-CPA and 11-hydroxyundecanoic acid or ricinoleic acid, when used as initiator/stabiliser in the absence of added conventional surfactant, produced stable monodisperse latices. Yet the potassium salt of the ester B derived from 4,4'-AB-4-CPA and 11-hydroxyundecanoic acid, when used as initiator/stabiliser in the absence of added conventional surfactant, failed to give a latex.

Nevertheless, all the esters derived from acid chloride I promoted bulk polymerisation except, of course, those esters which were insoluble in

styrene. Also, all the esters acted as effective initiators for emulsion polymerisation when a conventional surfactant was used as a stabiliser.

The esters derived from both acid chloride I and also acid chloride II and the fatty-alcohol ethoxylate condensates yielded stable latices when used in the emulsion polymerisation of styrene in the absence of added conventional surfactant. This is not surprising, since colloidal stability in this latter case is presumably conferred by the combination of hydrophobic and hydrophilic units present in the fatty-alcohol ethoxylates.

During the course of the investigation it was suddenly found to be impossible to prepare further batches of acid chloride I and the esters derived from it. Most subsequent attempts to prepare acid chloride I met with failure. Furthermore, little success was achieved in attempts made at elucidating possible structural differences between the two types of acid chloride that would account for the observed differences between them. Thus, all the detailed study of this type of initiator/stabiliser carried out in the latter part of this investigation used the esters derived from acid chloride II and the fatty-alcohol ethoxylates.

8.2. Conclusions drawn from the use of esters prepared from acid chloride II and fatty-alcohol ethoxylates as initiator/stabilisers.

8.2.1. Introduction. Acid chloride II, like acid chloride I, reacts with the free hydroxyl in the fatty-alcohol ethoxylates to form azo esters. Of the eight esters of this type derived from acid chloride II which were prepared, four -- namely, $FA(F.O)_{24}F.s$, $FA(F.O)_{30}F.s$, $FA(F.O)_{45}F.s$ and $FA(F.O)_{60}F.s$ --have been used as initiator/stabilisers for a detailed study of the kinetics of the emulsion polymerisation of styrene in the absence of conventional surfactant. Under all the conditions studied, all four esters produced stable, polydisperse polystyrene latices.

8.2.2. Summary of the conclusions. Four different shapes of conversion-time curves have been obtained when the esters prepared from acid chloride II and fatty-alcohol ethoxylates were used in the emulsion polymerisation of styrene in the absence of added conventional surfactant. These were as follows.

(i) Typical emulsion polymerisation curves (S-shaped) were given by $FA(EO)_{45}Es$ and $FA(EO)_{60}Es$ under all the conditions studied. $FA(EO)_{24}Es$ and $FA(EO)_{30}Es$ yield such curves when the temperature of polymerisation is below 50°C, and also at 50°C for high ester concentrations. Also, an increased volume of water (e.g., with a ratio of styrene to water of 40:145), conventional emulsion polymerisation curves were obtained. This is believed to be a consequence of the partial solubility of $FA(EO)_{24}Es$ and $FA(EO)_{30}Es$ in styrene. Thus, below 50°C the partition coefficient of the ester favours the water phase, whereas above 50°C the balance is towards the styrene. Increasing the volume of water or the concentration of ester is similar to increasing the amount of ester dissolved in the water phase and hence conventional emulsion polymerisation behaviour is favoured.

(ii) Curves resembling that of bulk polymerisation were obtained for the latices obtained when $FA(EO)_{24}Es$ and $FA(EO)_{30}Es$ were used as initiator/stabilisers at very low ester concentration or the volume ratio of styrene to water was low (e.g., 40:72 styrene-water ratio). Also, in some cases, this type of curve was obtained at intermediate temperatures. This behaviour is believed to be caused by the partial solubility of the esters in the oil phase.

(iii) However, at intermediate temperatures, a different-shaped curve can also be obtained; i.e., a curve consisting of two linear portions of decreasing slope. It is not a smooth bulk-like curve and electron micrographs show that the number of particles during the first portion of the curve changes, decreasing as polymerisation proceeds, but that the number of particles remains constant during the second straight portion. This first linear portion lasts up to approximately 40% conversion. Electron micrographs show that there are a great number of particles initially formed at the onset of the reaction but that considerable coagulation takes place, presumably because there is insufficient stabiliser in the water phase to cover their great surface area. This kind of curve is given by $FA(EO)_{24}Es$ and $FA(EO)_{30}Es$ at 50°C. The reason is believed to be that there is insufficient ester dissolved in the water phase to promote conventional emulsion polymerisation behaviour, and thus that the mechanism of polymerisation may resemble at the onset

bulk/suspension-like behaviour.

(iv) $FA(EO)_{24}Es$ and $FA(EO)_{30}Es$ also give a fourth type of curve, the beginning of which resembles bulk polymerisation; i.e., the rate decreases up to 20% conversion. After this, there is a linear portion whose slope varies according to the temperature of polymerisation and also according to the chain length of the ester. During this linear portion, the number of particles remains constant, the rate of reaction also remains constant, and thus the behaviour seems to resemble that of conventional emulsion polymerisation. However, because of the nature of the distribution of the ester between styrene and water at high temperatures, these esters prefer to dissolve in the oil and thus only a small fraction of the ester forms particles. After the limit of the linear portion is reached, there is an increase in the rate of polymerisation for about 10-15% further conversion. This acceleration is accompanied by a substantial increase in the number of particles. Finally, a faster constant-rate period is observed, before the rate begins to tail off at approximately 90% conversion. A possible explanation for the observed behaviour could be that at a given conversion of monomer to polymer, i.e., just before the acceleration occurs, the ester becomes insoluble in the polystyrene/styrene mixture and thus that it is ejected and redissolved in the water phase where new particles form. From this point onwards the behaviour of the polymerisation can be said to closely resemble conventional emulsion polymerisation. Even the curve obtained after acceleration has the characteristic S-shape. Unfortunately, time did not permit the detailed study of particle numbers after acceleration took place. This is an unfortunate omission, since this knowledge might shed some light on the reason for the unusually high conversions obtained before the rate began finally to decrease.

The complex curve described in section (iv) is obtained at temperatures above 50°C when $FA(EO)_{24}Es$ and $FA(EO)_{30}Es$ are used as initiator/stabilisers in the emulsion polymerisation of styrene in the absence of added conventional surfactant. $FA(EO)_{14}Es$ is believed to behave similarly at 50°C.

The conversion-time curves obtained when $FA(EO)_{45}Es$ and $FA(EO)_{60}Es$

were used as initiator/stabilisers resemble closely that for conventional emulsion polymerisation reactions in spite of the combination of the initiator and the stabiliser in one molecule. One of the divergences occurred at high temperatures when the polymerisation rate dropped. This could be due to the decrease in the ester solubility in water, and hence a tendency to dissolve in the oil phase. This is not surprising, since the ability of polyoxyethylene chains to form hydrogen bonds, and thus to favour the solubility of the molecule in water, decreases at high temperatures. The hydrogen bonds are destroyed because of the increase in the thermal motion of the system.

From what has been stated above, a drop in the number of particles would be expected as the temperature was increased above, e.g., 60°C for $FA(EO)_{45}Es$. Further investigation of the number of particles is required to confirm this prediction. The above suggestion is appealing also because the drop in rate in the case of $FA(EO)_{60}Es$ is observed at a higher temperature than in the case of $FA(EO)_{45}Es$. This is, of course, to be expected, since the hydrophilic end is longer in the former and thus a higher temperature would be required to reduce the solubility in water.

All four esters under certain conditions were found to give conversion-time curves which have a linear portion extending to unusually high conversions (up to 90% in some cases) before the rate of polymerisation begins to decrease. Since the monomer concentration within the particle must be decreasing well below this conversion, a second factor must be operating that balances the decrease in monomer concentration. This factor is thought to be the formation of new particles. That $FA(EO)_{24}Es$ and $FA(EO)_{30}Es$ do this is perhaps not too surprising. The same mechanism is also proposed for emulsion polymerisations initiated by $FA(EO)_{45}Es$ and $FA(EO)_{60}Es$. At high polystyrene concentrations, the ester that is dissolved inside the particle comes out and new particles form that, even if not in great numbers, help to counteract the effect of falling monomer concentration.

Reports in the literature that the fatty-alcohol ethoxylates have well-defined critical micelle concentrations (cmc) have been confirmed. However, no measurement of cmc has been possible for the esters derived

from fatty-alcohol ethoxylates and 4,4'-AB-4-CPA. Because of this, the mechanism of particle nucleation is thought to be homogeneous nucleation for reactions initiated by $FA(EO)_{24}Es$ and $FA(EO)_{30}Es$, and probably micellar or micellar/homogeneous nucleation for reactions initiated by $FA(EO)_{45}Es$ and $FA(EO)_{60}Es$. This is consistent with the observation that the esters investigated do not form micelles in quantities for critical micelle concentrations to be measurable.

It has also been found that the rates of decomposition of the azo group in the esters in water at different temperatures give activation energies comparable to the activation energies for the thermal decomposition of the sodium salt of 4,4'-AB-4-CPA and of AZBN. Also, at a given temperature the esters decompose at rates comparable to those for other azo compounds.

The sum of the orders of reaction with respect to initiator and to stabiliser concentrations predicted by Smith and Ewart ought to be unity. If one allows a certain margin for experimental error, the observed orders for reactions initiated by $FA(EO)_{45}Es$ and $FA(EO)_{60}Es$ could be regarded as being close to the theoretical expectation. However, the order of reaction obtained for reactions initiated by $FA(EO)_{24}ES$ and $FA(EO)_{30}Es$ is significantly higher than expectation, and it seems reasonable to conclude that this is due to the invalidity of some of the assumptions of the Smith-Ewart theory for reactions initiated by these particular compounds. One such assumption that does not hold in this particular case is that generation of radicals occurs solely in the aqueous phase.

Smith and Ewart predict an average number of radicals per particle of 0.5 during Interval II for case 2 kinetics. In this present research, it has been found that, in spite of the initiator/stabiliser being partially soluble in the oil phase as well as in the water phase and also acting as a stabiliser at the interface between the water and oil phases, the average number of radicals per particle is indeed close to 0.5. The high molecular weights of the polystyrenes produced support the finding of 0.5 radicals per particle, since a higher concentration of radicals in close proximity would result in rapid termination and hence in the formation of polystyrenes of lower molecular weight.

Also, it has been concluded that transfer of radicals from the propagating centres may be an important means of chain termination.

Although some reactions initially resemble bulk polymerisation, the final product is in all cases a latex, since the particle numbers are those typical for conventional emulsion polymerisation reactions. Also, the conversions are very high to have been obtained by a non-emulsion mechanism in the time given; and thus it must be concluded that bulk polymerisation is an insignificant contributor -- if a contributor at all -- in emulsion polymerisation reactions carried out using $FA(FO)_{24}Fs$, $FA(FO)_{30}Fs$, $FA(FO)_{45}Fs$ and $FA(FO)_{60}Fs$ as initiator/ stabilisers in the absence of added conventional surfactant.

8.3. Suggestions for further work. Unfortunately, because of lack of time, many questions have been left unanswered in this investigation, and many more questions arise from the research project itself. An attempt will be made in this section to enumerate a few of the most important areas where it is thought further research is desirable.

(1). Accurate particle-number determinations are essential for the elucidation of the mechanism of these emulsion polymerisation reactions, particularly in the earlier stages of polymerisation, when even electron micrograph techniques are not fully satisfactory. Light-scattering techniques could be used to investigate the mechanism of particle nucleation. This is particularly important for reactions initiated by $FA(FO)_{45}Fs$ and $FA(FO)_{60}Fs$, where it is not possible to draw definite conclusions from the present result.

(2). $FA(FO)_{45}Fs$ and $FA(FO)_{60}Fs$ give abnormally high conversions for the constant-rate period for most of the reactions investigated. It would be profitable to carry out a detailed study of the variation of particle number with conversion for reactions initiated by these compounds at higher temperatures, e.g., 65°C, and up to 90% conversion, in order to establish whether new nucleation of particles is responsible for the observed phenomenon. Furthermore, the same procedure but at lower temperatures, e.g., 50°C, ought to be carried out, since such behaviour is also observed at this temperature.

(3). It has been observed that reactions initiated by both $FA(EO)_{45}Es$ and $FA(EO)_{60}Es$ at very high temperatures, ca. 65°C, show a decrease in rate and in the number of particles with increasing conversion. It would be interesting to carry out a reaction initiated by $FA(EO)_{45}Es$ at 80°C, since this ester is soluble in water at that temperature. A further decrease in the rate and in the number of particles would be expected, perhaps, but, the question arises as to whether the shape of the conversion-time plots would remain similar to that for conventional emulsion polymerisation reactions.

(4). It would be interesting to re-investigate the effect of temperature upon reactions initiated by $FA(EO)_{24}Es$ and $FA(EO)_{30}Es$, but at a much higher volume ratio of water to styrene, e.g., a ratio of styrene:water of 40:225, in order to establish whether the unusual effect of acceleration and decrease of rate with increase in temperature is reduced.

(5). The emulsion polymerisation of styrene when an intermediate fatty-alcohol ethoxylate ester, e.g., $FA(EO)_{35}Es$ or $FA(EO)_{40}Es$, is used as initiator/stabiliser could help to make more complete the information which has been obtained in the course of these investigations.

(6). It would be of interest also to repeat some of the investigations of this project but using fatty-alcohol ethoxylates of the "Texofor B" type. The ethoxylates in this range have a hydrophilic portion of fixed size, the variable being the hydrophobic part.

(7). All the experiments performed in this investigation were carried out by dissolving the ester in the water and then adding the aqueous solution to the styrene. The alternative procedure of dissolving the esters in the styrene and then adding this solution to the water ought to be attempted, since interesting results might be obtained, particularly for the early stages of polymerisation, when equilibrium of the ester in both phases might not have been reached.

(8). 5.0 g of $FA(EO)_{14}Es$ per 40 ml of styrene at 50°C gave a very low rate of polymerisation. Also, the conversion-time curve was similar to that given by $FA(EO)_{24}Es$ and $FA(EO)_{30}Es$ at 55°C and above. An

increase in the amount of water, and an increase in the amount of ester, together with a decrease in the temperature of polymerisation, may yield a conversion-time curve of different shape.

(9). It has been concluded that the conversion at which new particles generate depends upon the polyoxyethylene chain length of the ester. Further investigation of the emulsion polymerisation of styrene using $FA(EO)_{14}Fs$ as initiator/stabiliser at 50°C might confirm or disconfirm the validity of the above prediction.

(10). Fractional creaming of the latices could be carried out in an attempt to separate the latex particles of different sizes, and an attempt could then be made to find out if the polymer contained in the new small particles is of different molecular weight to that contained in the older, larger particles.

(11). The effect of these initiator/stabilisers in the emulsion polymerisation of a more water-soluble monomer, such as methyl methacrylate, could be studied.

(12). Since it has been tentatively concluded that transfer of radicals from the polymerisation centres to other centres can be an important mode of chain termination, a labelled initiator could be used to try to establish whether transfer is indeed an important means of termination.

(13). Because of the amount of undecomposed initiator stabilising the polystyrene particles is considerable, the subsequent addition of a different monomer may result in polymerisation of the new monomer to yield a latex having core-shell-type particles; e.g., if butadiene monomer were added to a polystyrene latex, the final product would be expected to possess a hard core and a soft shell that might be of some industrial interest.

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